THE CRYSTAL STRUCTURES OF SOME MERCURY (II) COMPLEXES AND A TRIHALIDE COMPOUND.

Submitted to the University of Glasgow

For the Degree of Doctor of Philosophy

in the Faculty of Science

by

Ronald S. McEwen.

Chemistry Department

September, 1965.

P R E F A C E

I wish to thank Professor G.A. Sim and Professor J. Monteath Robertson for their instructive supervision over the years of my research.

I am also indebted to Drs. H. Mills and J.C. Speakman for their advice, and to the many crystallographic Programmers and others whose work made this research possible.

The financial support was supplied from the Department of Scientific and Industrial Research and latterly from the University of Glasgow in the form of an Assistant Lectureship.

SUMMARY

Chapter I reviews relevant structural knowledge of compounds containing mercury (II). Much of this material is to be found in a review by Deacon (1963), and will appear in a review by Grdenic (1965).

A detailed description of the solution of the structures of dichlorobisthioureamercury (II), dibromobisthioureamercury (II) and dichlorobisphenoxathiinmercury (II) comprises the first parts of chapters 2, 3 and 4. The structures are described in 2.2, 3.2 and 4.2. 4.3 discusses the implications of the structure of dichlorobisphenoxathiinmercury (II), and suggests an explanation for its visible absorption spectrum.

In chapter 5, a general discussion on the structures of mercury (II) complexes is presented. In the light of recent investigations, a useful way of rationalising the complicated co-ordinating habits of mercury (II) is illustrated. Consideration of the structures elucidated in this thesis falls naturally within this discussion.

Chapter 6 describes the solution and structure of the compound $(C_6H_5)_3$ $AsBr_3I$. The structure is not yet refined, and only a brief discussion is given.

The appendix sets out the main equations and the method of solution used in this thesis.

TABLE OF CONTENTS

Preface

Summary

Chapter		Page
1	The Structures of Mercury (II) Complexes	1
2	Dichlorobisthioureamercury (II)	
2.1	Solution of the Structure	5
2.2	Description of the Structure	18
3	Dibromobisthioureamercury (II)	
3.1	Solution of the Structure	21
3.2	Description of the Structure	28
4	Dichlorobisphenoxathiinmercury (II)	
4.1	Solution of the Structure	30
4.2	Description of the Structure	36
4.3	Discussion of the Structure	38
5	Discussion of the Structures	43
6	The Structures of Trihalide Ions	
6.1	Introduction	55

Chapter		Page
6.2	Solution of the Structure of $(C_6H_5)_3AsBr_3I$	62
6.3	Description of the Structure	72

Appendix

References

CHAPTER I

THE STRUCTURES OF MERCURY (II) COMPLEXES

1. THE STRUCTURES OF MERCURY (II) COMPLEXES.

Zn^{2+}, Cd^{2+}, Hg^{2+}, Cu^{+}, Ag^{+} and Au^{+} have complete d shells. Consequently, the stereochemistry of their compounds should, on a simple ionic theory, be determined by the size and charge of the ions. In particular, the larger ions should exhibit higher co-ordination numbers. Ag^{+} and Hg^{2+} are exceptional, however, in displaying a marked preference for two-fold co-ordination, or rather structures in which two ligands are closely bound to the metal, and four others are situated much further away, completing a distorted octahedron.

In this thesis attention is directed to the variation of co-ordination and stereochemistry of mercury (II) complexes with ligand types. The experimental work described here, is part of a broader programme, started in this laboratory, and continuing elsewhere.

Apart from the solitary example of the highly ionic mercuric fluoride (Wells, 1962), high co-ordination is unknown for mercury. Also, no example of completely regular octahedral co-ordination has been reported. Fourfold co-ordination is common. In two cases, almost completely regular tetrahedral co-ordination has been found. In the mercurichloride derivative of the alkaloid perloline, (Jeffreys et al., 1963), the $HgCl_4^{2-}$ anion is

quite isolated by the large organic molecule, and has suffered only minor distortions by the cation. In red mercuric iodide, the HgI_4^{2-} tetrahedra share edges (Huggins and Magill, 1927). Halogen bridging is a general feature in halomercurate structures. In most other structures containing four co-ordinate mercury, the polyhedron is extremely irregular.

Compounds, which from their stoicheiometries, might be expected to exhibit threefold co-ordination, have been shown to have distorted octahedral or tetrahedral co-ordination. However, some structures approximating closely to trigonal are known. Structures also exist in which Hg is closely surrounded by three ligands, and at a greater distance by two others. In table (A) is given a list of some known mercury structures, with their type of co-ordination and bond lengths.

Two explanations have been offered to account for the high incidence of linear structures in the solid state. The energy separation between the outermost s and p shells is greater for mercury than for zinc or cadmium. It is argued that it is energetically more favourable to construct two bonds using sp metal hybrids, than four using sp^3 metal hybrids (Nyholm,1961). However, it has also been pointed out that s - p

separation may not be great enough to account entirely for the mercury stereochemistry, and that d - s mixing is important in facilitating the formation of linear bonds (Orgel,1958).

Deviations from tetrahedral symmetry in four - co-ordinate complexes have been attributed to steric interaction. Branden (1964 (b)) has commented that there is a correlation between mercury-sulphur bond lengths and the co-ordination of the mercury atom in many complexes. He has concluded that the average bond length is approximately 2.34Å when the co-ordination is distorted octahedral (linear), and 2.55Å when it is tetrahedral or nearly so. In all the structures he has considered, the Hg - Cl distances have remained around 2.32Å, and he has further concluded that this bond length is relatively little altered by co-ordination changes of the mercury.

π - Bonding in mercury complexes is often possible if the ligand has suitable empty orbitals (Cotton,1960), and has been evoked to explain the stability order observed for the mercury halides (Ahrland,1956 and Ahrland and Chatt,1958). If the energy of hydration of the free halide ions is taken into account in assessing the relative stabilities of the solution species, the order is reversed, and conforms with expectation.

The structural data for solid compounds are not sufficiently advanced to enable conclusions regarding π - bonding to be drawn.

CHAPTER 2

DICHLOROBISTHIOUREAMERCURY (II)

2. DICHLOROBISTHIOUREAMERCURY (II).

2.1 Solution of the Structure.

The adduct of mercuric chloride with two molecules of thiourea $HgCl_2\ [(NH_2)_2CS]_2$ crystallises in colourless prisms. A crystal was mounted so that it could be rotated about the direction of its longest dimension. From oscillation, precession, and equi-inclination Weissenberg photographs, it was found to be orthorhombic, with unit cell dimensions: a = 12.79, b = 5.89, c = 6.44Å, the last axis corresponding to the elongated dimension of the crystal. The unit cell volume is 485.1$Å^3$, and assuming it to contain two formula units of $HgCl_2.[(NH_2)_2CS]_2$, the calculated density is 2.84 $gm.cc.^{-1}$.

The conditions governing possible reflections are: h 0 l present when h + l = 2n, h 0 0 present when h = 2n, and 0 0 l present when l = 2n. These conditions satisfy the space groups 31 and 59, p m n 2_1 and P m n m. They differ by a centre of symmetry. The numbers of general positions in these groups are four and eight respectively, and the choice between them is equivalent to placing the mercury atom and hence the complex on either one or two mirror planes. In the lower symmetry group, initially assumed, the m position is (0, y, z). The group has no fixed origin, and z can be chosen arbitrarly for one atom.

In addition to the systematic absences, the reflections are weak when h+k+l = 2n+1. These are clearly reflections to which the mercury does not contribute, since their intensities decrease more rapidly with increasing sin θ, than do those of the other reflections. Occupation of the m position, does not, in general, lead to additional conditions, but if y = 1/4, for the mercury, this atom will not contribute to the weak class of reflection. When h+l = 2n, the geometrical parts of the structure factor are

$$A = 4 \cos 2\pi hx. \cos 2\pi ky. \cos 2\pi lz.$$

$$B = 4 \cos 2\pi hx. \cos 2\pi ky. \sin 2\pi lz.$$

When h+l = 2n+1,

$$A = -4 \cos 2\pi hx. \sin 2\pi ky. \sin 2\pi lz.$$

$$B = 4 \cos 2\pi hx. \sin 2\pi ky. \cos 2\pi lz.$$

When h+l = 2n, and k = 2n+1, h+k+l = 2n+1, and A and B involve $\cos(\pi/2 \times \text{odd integer})$, which is identically zero. When h+l = 2n+1, and k= 2n, h+k+l = 2n+1, and A and B involve sin nπ, which is zero. Therefore F = 0 when h+k+l = 2n+1.

Also, when h+l = 2n and k = 2n, A and B involve $\cos n\pi = \pm 1$, and when h+l = 2n+1, and k = 2n+1, A and B involve $\sin(\pi/2 \times \text{odd integer}) = \pm 1$, so that when h+k+l = 2n, the mercury atom contributes fully.

Intensity data for the layers hk0 → hk5 were

estimated visually from equi-inclination Weissenberg photographs, taken with Cu Kα radiation (λ = 1.5418Å), using the multiple film technique (Robertson,1943). The interfilm scale factors of Rossmann (1956) were used. The layers were placed on approximately the same scale by comparison with the reflections of the layer h O l, which were obtained from timed-exposure, precession photographs, taken with Mo Kα radiation, (λ = 0.7107Å), again by visual comparison. Data reduction was carried out on the DEUCE computer for the Weissenberg series, and graphically for the precession series.

The 444 independent, non-zero reflections estimated, represent 80% of the total number of reciprocal lattice points contained in the octant of reciprocal space accessible to Cu Kα radiation.

Absorption was rather high (μ = 389.9 cm^{-1}), and the data were terminated at a point where many reflections were still of high intensity. Neglect of errors due to absorption later resulted in some anomalously low temperature factors.

From reflection conditions alone, the a and c axes are indistinguishable. They can be differentiated by inspection of the Patterson function as will be seen later.

The Patterson space group is P m m m. The unique volume a/2 x b/2 x c/2 was calculated in sections normal

to the c-axis. The four symmetrical vectors for P m n 2_1 are:-

$$(1/2 + 2x, \pm 2y, 1/2), \underset{1}{(1/2, 2y, 1/2)}, \underset{2}{(2x, 0, 0)}, \underset{3}{\quad}, \underset{4}{\quad}$$

and their centrosymmetric equivalents. Vectors (1) and (2) will, in general, occur on one mirror plane, (3) and (4) on two mirror planes, so the latter pair will be of double weight. The axis which contains vector peaks of the type (4), is the a-axis in P m n 2_1.

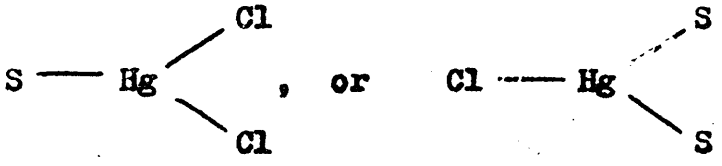
The most prominent feature of the Patterson function is a peak of height 0.87 times that of the origin, at (1/2, 1/2, 1/2). This confirms the mercury position as (0, 1/4, z). Secondly, all the major peaks lie on (or very near) the planes w = o and 1/2. This implies that to a close approximation, the space group is P m n m. The section at w = o is shown in figure (1).

Around the origin at a distance of about 2.5Å in the plane w = o, there is a hexagon of peaks of height 0.15 times that of the origin peak. This is close to the height expected for a Hg-Cl or Hg-S interaction. Above the origin, there extend a series of maxima and minima. These may have represented atomic vectors, but could also have well been due to the abrupt termination of the data along the c - axis. It was clear that a Hg-Cl or Hg-S vector could have been lost in a diffraction

minimum. Of the six peaks surrounding the origin, two are independent. Their positions are:

(A) (0.183, 0.158, 0.000), (B) (0.000, 0.417, 0.000)

To account for both these peaks, it must be taken that three atoms surround the mercury in this plane. Since sulphur and chlorine have similar atomic numbers, it was not possible to decide, at this stage, whether the structure was



This was settled when the light atoms were located at a later stage in the analysis.

The atomic positions from the Patterson map are:-

(1) (0.183, 0.408, 0.000)

(2) (0.000, -0.167, 0.000)

(The position (0.000, 0.667, 0.000) would be physically unreasonable).

They give rise to the following symmetrical vectors:-

I. (a) $(1/2 + 2x, \pm 2y, 1/2)$ (0.143, 0.184, 0.500)

(b) (1/2, 2y, 1/2) (0.500, 0.184, 0.500)

(c) (2x, 0, 0) (0.286, 0.000, 0.000)

2. (a) $(1/2 + 2x, \pm 2y, 1/2)$ (0.500, 0.334, 0.500)

In addition, the non-symmetrical S-Cl peaks were located.

The appearance of peak (c) above, implies that the axis of length 12.79Å, is indeed the a-axis in P m n 2_1, since no such vectors appear along the other axis.

To confirm these positions, structure factors were calculated using the mercury position only, with a temperature factor U = 0.009 $Å^2$. The agreement between observed and calculated structure factors was R = 0.28, over the set h+k+l = 2n. These Fs were used to compute a F_o synthesis and the resulting symmetrised map gave back the co-ordinates of the atoms already found. It also contained prominent diffraction ripples and failed to give any clear indication of the locations of the remaining atoms.

Now all structure factors, for which a non-zero value had been observed, were calculated using the co-ordinates:

	x	y	z	U $Å^2$
Hg	0.000	0.250	0.000	0.009
Atomic	0.183	0.408	0.000	0.013
no. = 17	0.000	-0.167	0.000	0.013

The overall agreement index was 0.30. 405 of these structure factors were used to compute a difference synthesis. The terms for which $\|F_o| - |F_c\| > 2\ |F_c|$ were rejected. The Fourier map revealed unambiguously

the light atom positions, and indicated that the temperature factor used for the mercury had been too low. The ripples around the mercury, had now largely disappeared, leaving a modest peak at (0, 1/4, 1/2). The co-ordinates given above were, for the moment, left unaltered, and the following added:

	x	y	z	U $\mathring{A}^2$
Atomic no. = 17	0.000	0.250	0.500	0.013

Recalculation of the structure factors of the layer hkl, resulted in a decrease in the disagreement factor R, from 0.341 to 0.322. The further addition of the co-ordinates:

	x	y	z	U $\mathring{A}^2$
C	0.270	0.162	0.000	0.025
N	0.236	0.969	0.000	0.025
N	0.362	0.237	0.000	0.025

and recalculation of hkl structure factors, brought R to 0.319. The slight decreases in R, were taken as indication that the structure was essentially correct. The light atom positions showed that the atom at (0.183, 0.408, 0.000) was the sulphur atom.

As a final check on the correctness of the structure, and more for interest than necessity, a partial Patterson synthesis was computed. Two atoms, mercury and one other, have co-ordinates (0, 1/4, z),

and therefore make no contribution to the reflections h+k+l = 2n+1. This class alone was used to compute the Patterson synthesis. This map displayed vectors only between the contributing atoms. If it had been necessary to obtain detailed information from this synthesis, the contribution made by the atoms at (0, 1/4, z) to the set h+k+l = 2n could have been subtracted from the observed values, and these too included in the calculation. However, sufficient data were used to permit clear identification of all the vectors involving the light atoms with those of intermediate weight. The section at w = 0 is shown in figure (2) with some of the principal interactions marked. All large peaks were accounted for on the basis of the two intermediate sized atoms and this confirmed that one chlorine is indeed at (0, 1/4, z).

To within very close limits all the atoms lie on the planes z = 0, 1/2, and at this stage the assignment of the space group was reconsidered. To a first approximation, all the atoms were placed so as to satisfy the centrosymmetric space group P m n m.

The reflections can be split into four classes:

(1)	$h+l = 2n$	(2)	$h+l = 2n+1$
	$k = 2n$		$k = 2n+1$
(3)	$h+l = 2n$	(4)	$h+l = 2n+1$
	$k = 2n+1$		$k = 2n$

Classes (3) and (4) do not receive contributions from the mercury or chlorine[2] atoms. For class (1)

$A \propto \cos 2\pi lz$ and $\partial A/\partial z \propto -\sin 2\pi lz$.

For class (2), $A \propto \sin 2\pi lz$ and $\partial A/\partial z \propto \cos 2\pi lz$. If $z = 0$ initially, class (1) will be ineffective in removing the atoms from the pseudo-mirrir plane. If the atoms were to be given small random shifts from the plane, the derivatives, $\partial A/\partial z$, would become finite, but A would be independent of the direction of the shift in z, since A is symmetric with respect to inversion in the z axis. The B part of F would be small and therefore of little importance in refinement from the pseudosymmetrical arrangement.

For atoms whose true z co-ordinates differ from zero, the effect on class (1) reflections could be simulated by a high component of the anisotropec temperature factor, B_{ss} in that direction. B_{ss} and z

might then be expected to be highly correlated. In other words, to refine the parameters correctly by least squares, consideration must be taken of the terms

$$\sum w \left(\frac{\partial |F_c|}{\partial z} \right) \left(\frac{\partial |F_c|}{\partial U_{ss}} \right)$$

in the normal equations. This would require at least a 9x9 block diagonal solution.

On the Rollett programme for the DEUCE computer, on which the structure was refined, the terms calculated are a 3x3 matrix for each atomic position, and a 6x6 matrix for each atomic vibration (and a 2x2 matrix for the scale factor).

These remarks only apply to class (1) reflections, but since these constitute a half of the strong class, it was decided to refine the structure initially in the centrosymmetric space group, and not to attempt to break the symmetry unless chemical considerations should warrent it.

The space group was raised to P m n m, and the origin moved to the centre of symmetry at (- 1/4, 0, - 1/4), so that the phases were now restricted to 0^c or π^c. To maintain consistency, the non-standard orientation was chosen. Figure (3) shows (a) the space group P m n 2_1 (standard orientation), (b) P m n m with the

origin at m m, and (c) P m n m with the origin at $\bar{1}$. In the latter, all the atoms lie on the special positions:-

x,y,1/4: $\bar{x},\bar{y},3/4$: 1/2-x,y,1/4: 1/2+x,$\bar{y}$,3/4

The mercury and chlorine atoms have x = 1/4, and so occupy the m m position.

Since all the atoms lie in special positions, the components of the temperature factors are restricted in the following way. For mercury and chlorine atoms, all $U_{ij} = 0$ $(i \neq j)$. For other atomsin positions of m symmetry, $U_{23} = U_{31} = 0$. To obtain these results, consider the equivalent indicies, $h_s k_s l_s$ for the space group. For P m n m, they are:

$$hkl \quad \bar{h}kl \quad h\bar{k}l \quad \bar{h}\bar{k}l \quad \text{etc.}$$

Write the anisotropic temperature factor exponent as:

$$b_{11}h^2 + b_{22}k^2 + b_{33}kl + b_{31}lh + b_{12}hk ,$$

where $b_{11} = 2\pi^2 a^{*2} U_{11}$, . . . etc

and $b_{33} = 2\pi^2 b^* c^* (2 U_{33})$,... etc.

For an atom in a special position, which is transformed into itself by a symmetry operation corresponding to the set of equivalent indices, $h_s k_s l_s$,

$$b_{11}h^2 + \ldots = b_{11}h_s^2 + \ldots$$

Hence for atoms on the mirror plance perpendicular to c, in P m n m,

$$b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{31}lh + b_{12}hk$$

$$= b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}k(-l) + b_{31}(-l)h + b_{12}hk.$$

i.e. $b_{23} = b_{31} = 0$

Similarly for atoms lying on the mirror plane perpendicular to the a-axis, $b_{12} = b_{31} = 0$, so for atoms in the m m position, all bij = 0, $(i \neq j)$.

There was no facility on the Rollett programme for the DEUCE computer to keep parameters constant during least-squares refinement, and the z co-ordinates and zero temperature factors had to be returned to their original values in between cycles.

Before refinement was started, the various layers of Fs were placed on the same scale by making $\sum k |F_o| = \sum |F_c|$ for each layer. The inter-layer scaling factors, k, must be strongly correlated with the temperature factors. At various points in the refinement, the inter-layer scale factors were altered to maintain the best agreement between observed and calculated structure factors. At the conclusion of refinement, the scale factors were found to differ by not more than 6% from those determined by scaling against the correlating series F(hOl).

Two weighting schemes were built into the Rollett programme. The one chosen made the root of the weight $\sqrt{w} = 1$ if $|F| < |F \text{ average}|$, and $\sqrt{w} = |F \text{ average}| / |F|$ if $|F| > |F \text{ average}|$. This downweighted strong reflections which would be most affected by absorption and extinction.

The refinement converged at R = 0.183 after 7 cycles. In view of the quality of the data, and the more or less reasonable values of bond lengths and angles, it was decided to conclude the investigation at this stage, with the main structural features clearly established, though it was recognised that there may be small departures from the higher symmetry.

A final difference Fourier synthesis showed only minor and random fluctuations of density.

2.2 Description of the Structure.

To the extent to which the space group approximates to P m n m, the symmetry of the mercury complex is m m, or C_{2v}. This requires that all the atoms lie in special positions on the planes z = 1/4 and 3/4. The mercury is immediately surrounded by five atoms. A chlorine and two sulphur atoms lie in one plane with the mercury, and two other chlorines are almost linearly co-ordinated to the mercury, the mercury-chlorine bonds being normal to the plane. These two chlorines are related to one another by the mirror normal to the c-axis, and the two sulphur atoms are inter-related by the second mirror plane normal to the a-axis. This plane contains the mercury and the chlorine atoms.

The distances between the mercury and atoms in the 'c' plane are shorter than the distance between mercury and the other chlorine atoms. Bond angles and lengths are given in tables (4,5) and illustrated in figure (4). The dimensions of the thiourea ligands are, to within the limited accuracy of location of the light atoms, the same as those found by Kunchur and Truter (1958) in crystalline thiourea. The angle subtended at the sulphur atom is, as might be expected, near to the tetrahedral angle.

The thiourea ligands are so positioned, that one

nitrogen atom of each, N(1), approaches the chlorine more closely bonded to mercury, to within 3.23 Å. The Cl-N-C angle is 122.6°, so it may be inferred with some confidence that hydrogen bonds exist. This is, of course, subject to the assumption that the hydrogen atoms lie in the plane of the chlorine, nitrogen and carbon. Therefore, the chlorine would appear to be doubly hydrogen bonded. Two six membered chelate rings are completed by these bonds. The other hydrogen on N(1) is not suitably placed to form a hydrogen bond.

The other nitrogen atoms, N(2), of the thiourea groups, could possibly bridge adjacent chlorine atoms, which are less closely bonded to mercury, with weak hydrogen bonds. The Cl-N-C angles are in this case, rather further removed from the expected H-N-C angle, and the inference of hydrogen bonding, consequently less certain.

The situation is rather similar to that in the structure of dichlorotetrakisthioureanickel, (Truter,1963) in which the chlorine atoms are also doubly hydrogen bonded. The N...Cl distance is the same (3.23 Å) as in dichlorobisthioureamercury (II).

The structure then, consists of an infinite array of parallel, planar $ClHg[(NH_2)_2CS]_2$ groupings, linked normally to the planes by symmetrical, chlorine-bridging

bonds to the mercury. Figure (5) shows the structure projected down the c-axis. (Some symmetry elements have been omitted from this drawing to avoid obscuring certain atoms).

Figure 1.

DICHLOROBISTHIOUREAMERCURY (II). The three-dimensional Patterson function. Section at w = 0, P(u,v,0). The contour levels are arbitrary.

Figure 1.

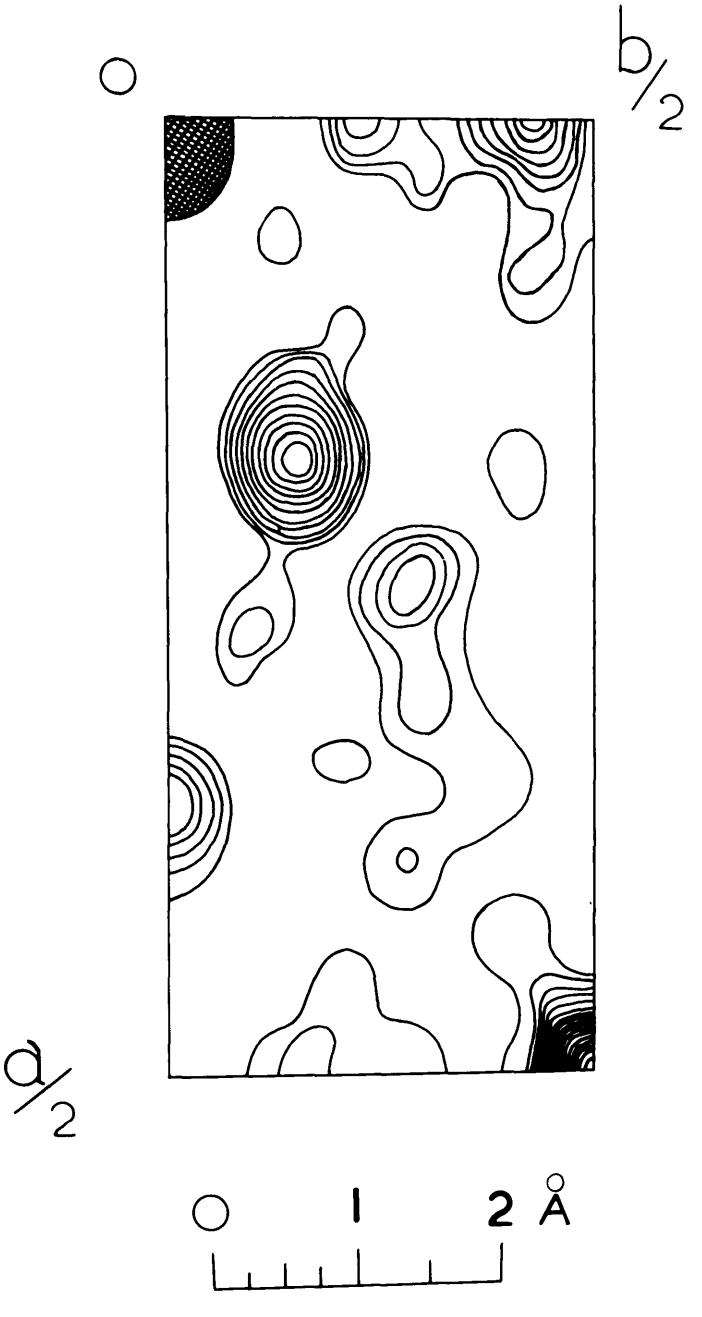


Figure 2.

DICHLOROBISTHIOUREAMERCURY (II). The three-dimensional partial Patterson function. Section at w = 0, Pp(u,v,0). The contour levels are arbitrary.

Figure 2.

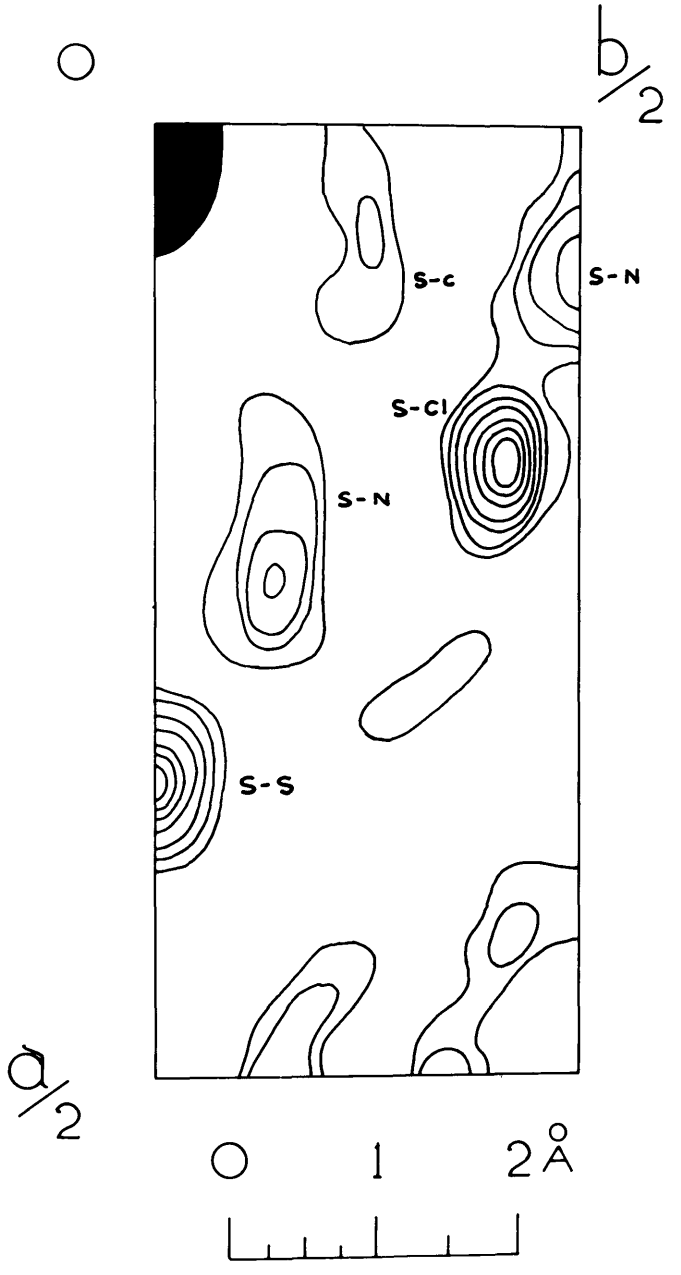
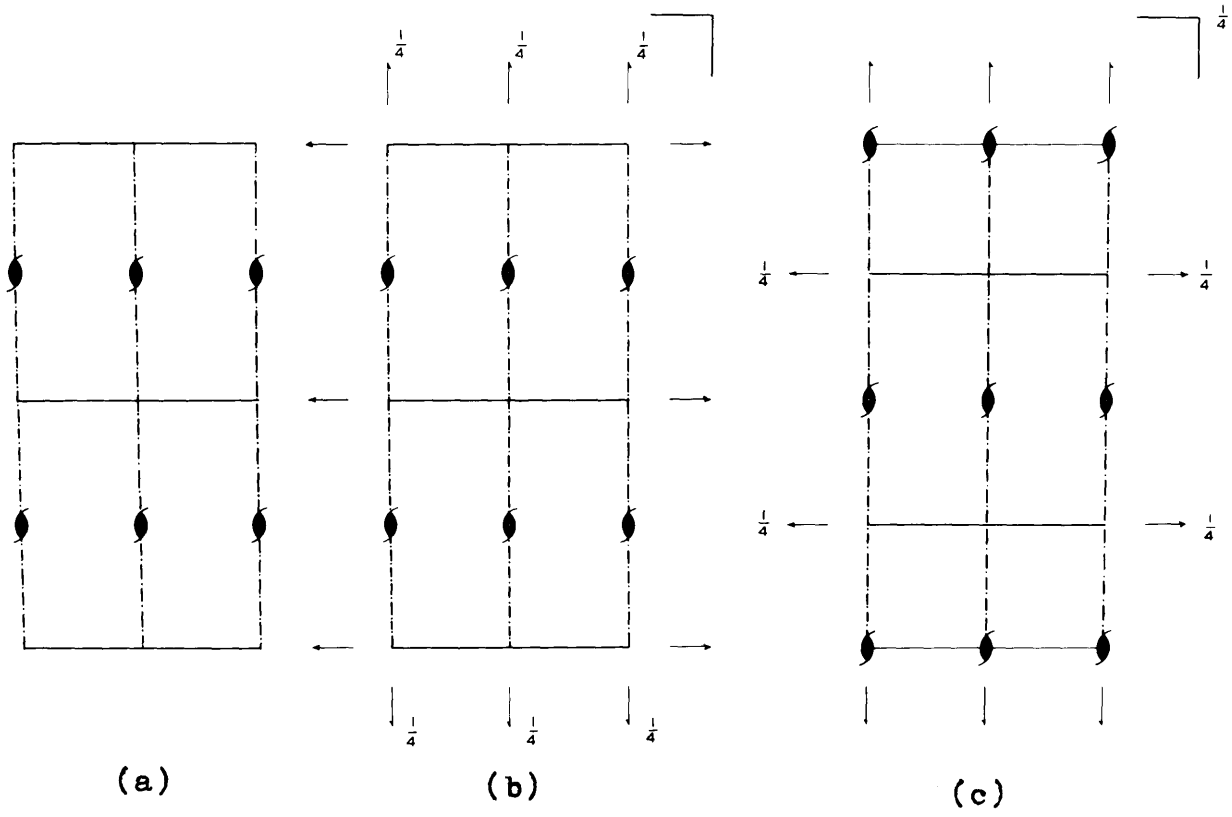


Figure 3.

The symmetry elements of the space groups (a) $Pmn2_1$, (b) Pmnm with origin at mm$\bar{1}$ and (c) Pmmm with origin at $\bar{1}$.

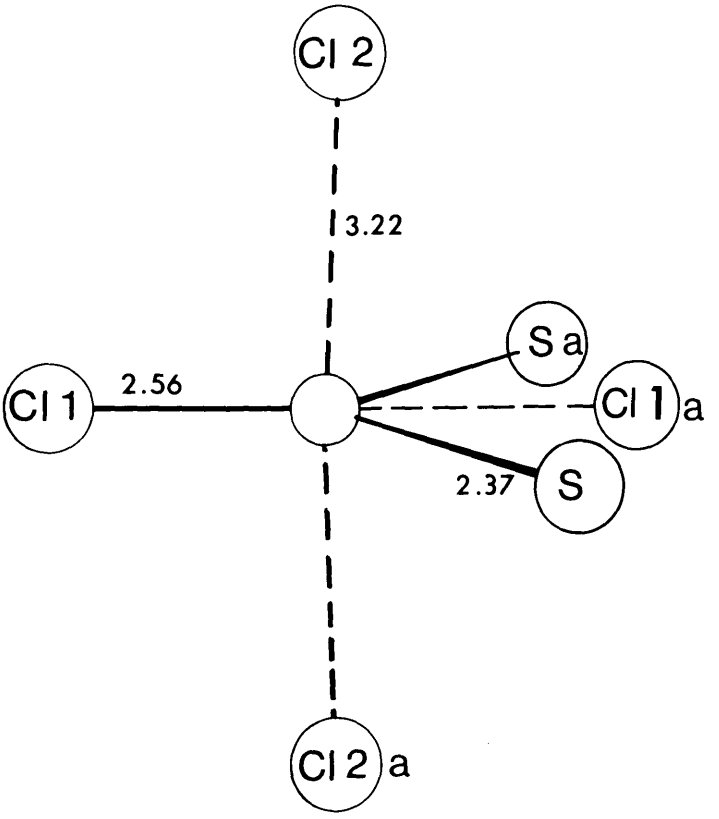

1/4
1/4
1/4
1/4
1/4
1/4
1/4
1/4
1/4
1/4
1/4
1/4
(a)
(b)
(c)

Co-ordinates of Equivalent Positions for Pmnm.

Origin at $\bar{1}$ at $\overline{1/4}$, 0 $\overline{1/4}$ from mnm.

1	x,y,z;	1/2-x,y,z;	x,y,1/2-z;	1/2-x,y,1/2-z;
	$\bar{x},\bar{y},\bar{z}$;	1/2+z,$\bar{y}$,$\bar{z}$;	$\bar{x}$,$\bar{y}$,1/2+z;	1/2+x,$\bar{y}$,1/2+z.
m	x,y,1/4;	$\bar{x}$,$\bar{y}$,3/4;	1/2-x,y,1/4;	1/2+x,$\bar{y}$,3/4.
m	1/4,y,z;	3/4,$\bar{y}$,$\bar{z}$;	1/4,y,1/2-z;	3/4,$\bar{y}$,1/2+z.
$\bar{1}$	0,1/2,0;	1/2,1/2,0;	0,1/2,1/2;	1/2,1/2,1/2.
$\bar{1}$	0,0,0;	1/2,0,0;	0,0,1/2;	1/2,0,1/2.
mm	1/4,y,3/4;	1/4,$\bar{y}$,1/4.		
mm	1/4,y,1/4;	3/4,$\bar{y}$,3/4.		

Figure 4.



The immediate environment

of the mercury atom

Figure 5.

DICHLOROBISTHIOUREAMERCURY (II). Projection of the structure down the $\underline{c}$-axis. Possible hydrogen bonding is indicated by dashed lines.

Figure 5.

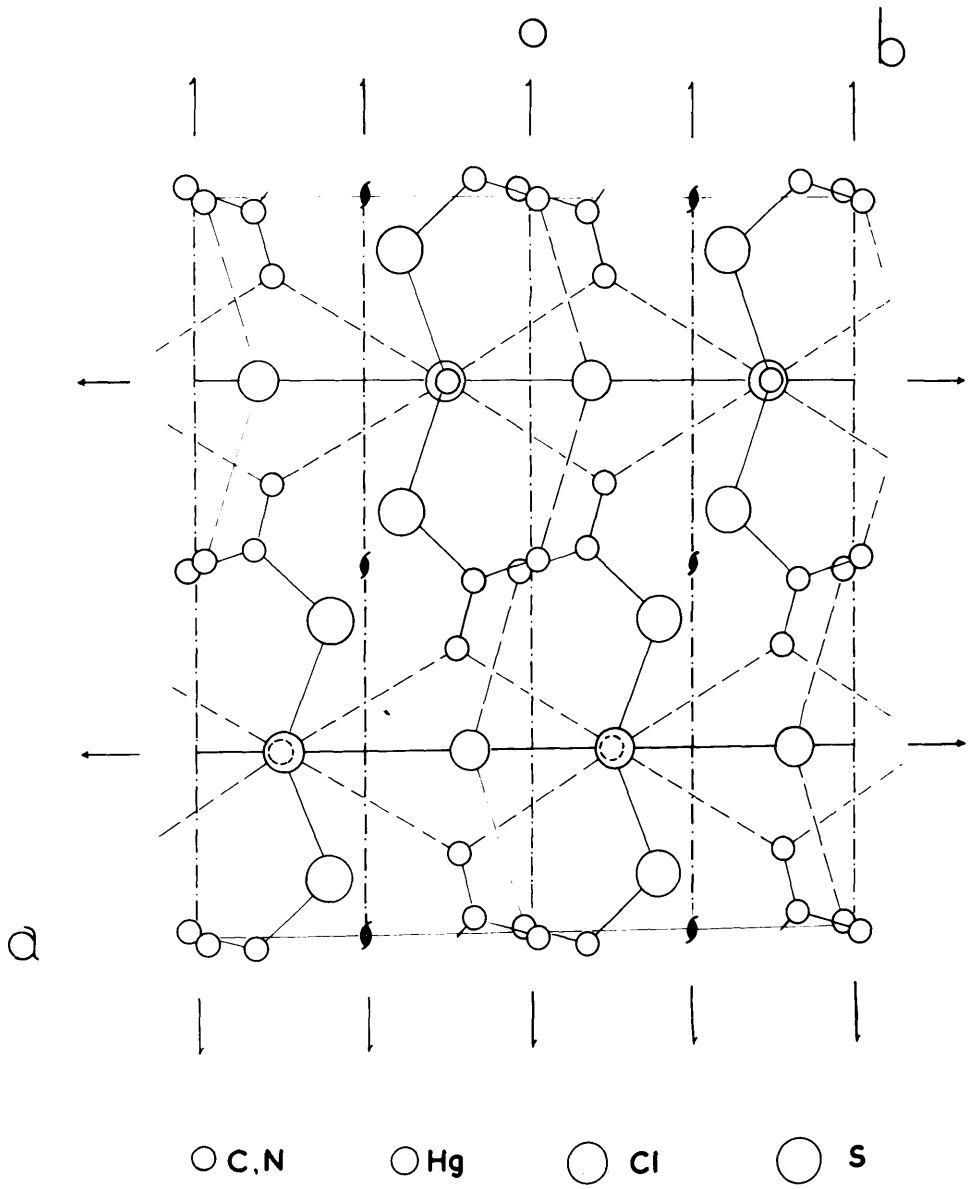


TABLE (I)

DICHLOROBISTHIOUREAMERCURY (II)

Fractional Co-ordinates

Atom	x	y	z
Hg	-0.25000	0.25135	-0.25000
Cl(1)	-0.25000	-0.18386	-0.25000
Cl(2)	-0.25000	0.25678	0.25000
S	-0.07607	0.39202	-0.25000
C	0.02115	0.17179	-0.25000
N (1)	-0.00716	-0.03338	-0.25000
N (2)	0.11005	0.21869	-0.25000

TABLE (2)

Estimated Standard Deviations of Fractional Co-ordinates.

Atom	σ (x)	σ (y)
Hg	-	0.00037
Cl(1)	-	0.00344
Cl(2)	-	0.00332
S	0.00109	0.00228
C	0.00353	0.00888
N (1)	0.00383	0.00806
N (2)	0.00811	0.00977

TABLE (3)

DICHLOROBISTHIOUREAMERCURY (II)

Anisotropic Thermal Parameters ($Å^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}
Hg	0.0190	0.0003	0.0297	-
Cl(1)	0.0139	0.0003	0.0021	-
Cl(2)	0.0449	0.0220	0.0375	-
S	0.0219	0.0003	0.0272	0.0016
C	0.0109	0.0003	0.0003	0.0036
N(1)	0.0261	0.0106	0.0441	0.0023
N(2)	0.0541	0.0004	0.1541	0.0091

TABLE (4)

DICHLOROBISTHIOUREAMERCURY (II)

Interatomic Distances and Estimated Standard Deviations (Å)

Atoms	Distance	
Hg - Cl(1)	2.563	(0.020)
Hg - Cl(1)(a)	3.328	(0.020)
Hg - Cl(2)	3.220	(0.008)
Hg - S	2.374	(0.014)
S - C	1.80	(0.05)
C - N(1)	1.26	(0.07)
C - N(2)	1.17	(0.11)
N(1) - N(2)	2.11	(0.09)
S - N(1)	2.66	(0.05)
S - N(2)	2.59	(0.07)
Cl(1) - N(1)	3.23	(0.05)
Cl(2)(c) - N(2)	3.32	(0.08)
Cl(2)(b) - N(■2)	3.57	(0.07)

TABLE (5)

DICHLOROBISTHIOUREAMERCURY (II)

Interbond Angles and Estimated Standard Deviations

Cl(2) - Hg - Cl(2)(a)	178.9°	(0.5°)
Cl(1) - Hg - Cl(2)	90.6°	(0.3°)
Cl(1) - Hg - S	110.5°	(0.3°)
Cl(2) - Hg - S	89.8°	(0.1°)
S - Hg - S(a)	139.0°	(0.2°)
Hg - S - C	113.4°	(1.7°)
S - C - N(1)	119.5°	(3.8°)
S - C - N(2)	120.1°	(4.8°)
N(1) - C - N(2)	120.4°	(5.0°)
C - N(1) - Cl(1)	122.6°	(3.5°)
C - N(2) - Cl(2)(b)	133.7°	(4.9°)
C - N(2) - Cl(2)(c)	108.9°	(4.2°)

The dependent atoms referred to in tables (4) and (5) are:

	x	y	z
Cl(1)(a)	-0.25000	0.81614	-0.25000
Cl(2)(a)	-0.25000	0.25678	-0.75000
Cl(2)(b)	0.25000	0.74322	-0.25000
Cl(2)(c)	0.25000	-0.25678	-0.25000
S(a)	-0.42393	0.39202	-0.25000

TABLE (6)

h	k	F_o	F_c
0	1	58.2	63.2
		49.7	- 44.5
0	2	51.5	- 47.0
		53.4	57.4
		54.8	- 42.5
0	3	49.5	- 55.9
		46.7	- 42.9
		36.3	29.3
0	4	63.5	65.9
		66.0	- 82.0
		69.8	60.4
0	5	67.4	- 76.1
		61.2	60.2
		42.1	- 42.2
0	6	77.7	- 88.4
		77.7	77.7
		66.3	- 56.9
0	7	49.3	59.4
		44.7	- 47.9
		27.6	36.3
0	8	59.4	63.2
		49.6	- 56.5
		37.0	43.0
0	9	30.4	- 32.9
		24.0	27.9
		15.9	- 20.7
0	10	44.6	- 46.7
		40.3	43.3
		25.4	- 34.6
0	11	43.6	52.4
		33.5	- 44.7
		23.2	33.5
0	12	47.0	54.0
		38.4	- 50.1
0	13	24.7	- 30.6
		18.0	26.6
0	14	22.7	- 28.3
		21.1	26.1
		16.0	- 20.9
0	15	16.1	22.4
		16.6	- 20.5
0	16	27.2	29.5
1	0	37.1	80.2
		15.4	34.9
1	1	45.2	79.5
		5.7	9.0
		58.8	- 65.6
		3.3	- 2.7
		43.1	46.6
1	2	25.5	- 27.6
		18.8	25.9
		12.7	- 17.3
1	3	47.0	- 67.3
		24.2	25.3
		48.6	56.1
		16.4	- 17.3
		33.1	- 37.0
1	4	11.1	11.7
		20.1	20.5
		30.2	34.1
		20.0	- 17.2
		25.3	- 31.0
		11.3	12.4
1	5	22.9	22.0
		64.3	66.7
		7.9	6.0
		53.5	- 53.7
		7.2	- 4.4
		42.2	41.3
		4.5	2.7
1	6	24.6	18.0
		39.2	- 50.3
		19.5	- 15.2
		35.9	39.2
		12.3	11.2
		26.0	- 25.9
1	7	40.1	- 53.9
		46.6	49.3
		29.9	- 37.5
1	8	21.0	17.4
		30.8	31.2
		18.5	- 15.7
		27.5	- 24.4
		13.0	12.5
		17.4	15.9
1	9	36.6	38.8
		13.2	- 12.1
		30.6	- 29.3
		9.4	10.3
		19.4	21.0
		7.8	- 7.8
		25.0	- 27.2
		19.0	22.9
		17.4	- 15.9
1	11	43.1	- 47.7
		7.5	- 4.3
		35.3	42.5
		3.6	3.5
		26.3	- 31.9
1	12	24.0	28.9
		17.3	- 24.2
		13.4	17.1
1	13	23.9	25.4
		4.3	- 2.3
		19.2	- 23.0
		17.4	17.2
		5.4	- 6.3
		15.1	- 17.9
		8.0	5.9
		13.6	14.7
		5.3	- 4.8
		11.7	7.0
		19.6	- 20.8
		6.4	5.8
		26.5	19.2
		9.1	- 5.2
		23.8	16.1
		42.0	- 40.4
		22.8	- 25.8
		11.7	7.0
		18.9	20.4
		37.7	- 52.5
		8.4	- 15.1
		31.1	- 30.1
		59.5	54.4
		19.7	22.6
		49.7	- 49.3
		15.3	- 14.6
		23.7	34.1
		39.2	44.2
		4.2	- 3.9
		76.5	- 81.9
		58.6	56.4
		16.0	- 16.0
		64.2	- 73.2
		17.8	12.5
		50.6	56.7
		8.6	- 7.3
		40.6	- 39.1
		54.2	- 60.8
		3.8	- 2.2
		56.2	63.6
		38.2	- 43.2
		25.7	- 24.3
		35.8	51.1
		18.7	21.6
		29.4	- 41.7
		12.5	- 17.0
		25.3	29.7
		56.1	71.2
		45.5	- 63.4
		14.7	- 18.6
		30.0	47.2
		13.6	14.8
		6.9	8.8
		36.2	- 46.3
		5.2	- 7.7
		29.5	41.9
		27.2	- 31.5
		54.3	- 70.6
		6.6	5.2
		44.4	54.0
		7.2	- 3.7
		28.2	- 41.8
		27.2	41.6
		28.7	- 35.5
		33.9	26.0
		43.8	49.6
		5.6	4.8
		33.4	- 46.0
		25.8	37.0
		11.4	10.6
		30.8	- 38.9
		12.0	- 10.0
		29.2	33.0
		7.3	8.4
		32.5	- 24.9
		29.4	- 36.0
		12.8	- 13.9
		33.8	33.4
		9.6	11.8
		24.9	- 26.7
		6.8	- 9.5
		4.0	- 7.2
		28.4	28.0
		5.3	6.8
		27.6	- 24.2
		4.0	- 6.2
		42.9	37.1
		7.2	- 4.4
		44.4	- 34.4
		7.0	3.5
		5.1	- 3.4
		31.8	- 27.7
		5.5	3.2
		3.3	- 2.6
		28.2	- 41.7
		34.0	32.2
		13.8	- 21.1
		67.4	- 62.5
		5.2	2.1
		48.6	53.4
		41.5	- 40.4
		20.9	17.1
		61.6	51.4
		16.2	- 12.5
		50.2	- 42.5
		9.2	10.5
		27.6	29.5
		101.2	82.5
		31.4	- 21.3
		85.9	- 72.4
		23.8	16.7
		57.8	52.4
		13.2	- 13.1
		14.3	- 5.8
		49.4	- 49.4
		8.3	4.2
		47.0	42.1
		7.6	- 6.9
		33.7	- 30.5
		60.4	- 50.4
		57.6	- 44.9
		31.6	- 33.0
		24.2	27.2
		20.6	- 21.8
		49.3	- 41.8
		11.0	- 7.5
		49.3	- 41.8
		8.8	7.8
		30.2	32.6
		9.7	- 7.7
		12.6	- 9.6
		50.5	- 49.3
		13.8	9.0
		39.5	40.9
		7.8	- 7.5
		43.9	- 29.1
		53.6	- 54.2
		8.1	- 7.3
		59.1	49.6
		6.1	- 5.6
		24.0	- 25.2
		25.9	18.3
		35.5	29.7
		3.5	- 6.1
		28.8	- 26.8
		4.6	5.7
		23.7	20.3
		24.2	- 20.2
		19.0	17.4
		48.2	- 30.0
		43.2	28.4
		11.4	8.9
		38.2	28.7
		11.2	- 8.5
		24.6	27.5
		51.1	52.7
		11.6	- 9.0
		29.4	- 36.0
		19.8	21.4
		3.6	- 2.7

CHAPTER 3

DIBROMOBISTHIOUREA[illegible]

3. DIBROMOBISTHIOUREAMERCURY (II)

3.1 Solution of the Structure.

Dibromobisthioureamercury (II), $HgBr_2[(NH_2)_2CS]_2$, was prepared by admixture of cold aqueous solutions containing mercuric bromide and thiourea in the ratio 1:2. The white complex precipitated slowly from the dilute solution, and was recrystallised from water. It was analysed for nitrogen content. Calculated for $HgBr_2C_2N_4H_8S_2$; N, 10.93%; found N, 10.92%. A well developed crystal, with dimensions, 0.018 x 0.020 x 0.05 cm, was mounted to rotate about the direction of its longest dimension. The crystal data obtained from oscillation, precession and Weissenberg photographs are: M = 512.69, monoclinic, a = 13.03, b = 6.19, c = 6.31 Å, $\gamma = 90°18'$; U = 510.0 $Å^3$; $D_c = 3.34$ g.cm.$^{-3}$; Z = 2; F(000) = 460.

From the precession photographs of the zones (h0l) and (0kl), it was observed that the (00l) reflections are only present when l is even. There are no other systematic absences. The space group is therefore $P2_1$ or $P2_1/m$ if the mercury atom occupies a special position. However, when h+k+l = 2n+1, the (hkl) reflections are weak. The (h0l) reflections are in fact extremely weak when h+l = 2n+1.

In view of the close similarity in the cell

dimensions, chemical formula, and intensity distribution between the dichlorothioureamercury (II) and the dibromothioureamercury (II), it was expected that the structures would differ very little, though they are not isomorphous.

The weak class of reflection can be explained by placing the mercury in the bromo-compound, in a position corresponding to that in the chloro-compound. For, if the mercury has co-ordinates (1/4, 3/4, 1/4), and the space group is assumed to be $P2_1/m$,

$$A = 4 \cos 2\pi(hx + ky) \cos 2\pi lz$$

$$\text{for } l = 2n,$$

i.e.
$$A = 4\left(\cos h\frac{\pi}{2} \cos k\frac{\pi}{2} \cos l\frac{\pi}{2} - \sin h\frac{\pi}{2} \sin k\frac{\pi}{2} \cos l\frac{\pi}{2}\right)$$

and for l odd, $A = -4 \sin 2\pi(hx + ky) \sin 2\pi lz$

The particularly weak reflections (h0l) when $h+l = 2n+1$, are a result of the extremely close correspondence in the (001) project of the structure with that of the chloro-compound.

Three-dimensional data were collected on a Hilger-Watts linear diffractometer, using a Hilger FT 165 scintillation counter and pulse height discrimination. The radiation used was Mo Kα, and the

balanced filter materials were Zr and Sr. A hemisphere of reciprocal space was investigated, and the (hkl) and ($\bar{h}\bar{k}$l) reflections averaged. A total of 1458 non-zero reflections were collected in the layers hk0 to hk7.

Initially, we had to assume that there was no symmetry at all about the mercury atom, although a mirror plane normal to the c axis was considered likely by analogy with the chloro-compound. However, the approximation of cell to orthorhombic, and the dominating influence of a very heavy atom in a special position, imposes pseudo m m m symmetry on the structure.

The Patterson space group is P 2/m. The volume $\frac{a}{2} \times b \times \frac{c}{2}$ was computed. Again a large peak at (1/2, 1/2, 1/2) confirmed the mercury position. A peak of height 0.25 at (0.020, 0.458, 0.000) is repeated at (-0.020, 0.542, 0.000) by the two-fold axis at(0, 1/2, z). This is of the expected height for a Hg-Br interaction (2800/9438 = 0.30) and occurs 2.8 Å from the origin, the shorter distance being taken. If this is a Hg-Br interaction, the co-ordinates of a bromine atom are therefore:

Br(1) (0.270, 0.208, 0.250),

in which case, a symmetrical Br-Br vector should occur at (0.540, 0.416, 1/2). This is close to the main Hg-Hg interaction, but a peak of height 0.1 times that

of the origin was found. The calculated height of a Br-Br peak is 0.13. The Hg-Hg peak is surrounded by a deep trough, and when the depth of this is taken into consideration, the observed peak height becomes 0.14.

A third major peak appears at (1/2, 1/2, 0), rather elongated in the x direction. Its height of 0.30 indicates that it is a double Hg-Br interaction. The second bromine position is therefore:

	Br(2)	(0.750, 0.250, 0.250) x,y,z
or, of course	Br'(2)	(0.250, 0.750, 0.750) $\bar{x},\bar{y}$,1/2+z

It was now possible to pick out the Hg-S vectors by analogy with the chloro-compound.

The positions were: (Hg = 1/4, 3/4, 1/4)

	Hg - S(1)	(0.173, 0.133, 0.000)
	S(2)- Hg	(0.170, 0.944, 0.122)
giving	S(1)	(0.077, 0.617, 0.250)
and	S(2)	(0.420, 0.704, 0.372)

Structure factors were calculated on the basis of mercury only, with a temperature factor, $B_{iso} = 8\pi^2 U_{iso} = 0.87$ Å^2. Over these reflections for which h+k was even, and l = 0, the agreement between observed and calculated values was R = 0.243. These terms were used to compute a symmetrised, projection Fourier - $P2_1/m$, with additional centres at (1/4, 1/4) and (1/4, 3/4) etc., which served to check the conclusions of the Patterson.

A three-dimensional structure factor calculation with these atoms, gave an overall R = 0.274, and a F_o Fourier synthesis gave improved co-ordinates and the positions of a carbon and two nitrogen atoms of one thiourea group. The three remaining light atoms were not obvious. A suitable light atom peak occured at (0.591, 0.751, 0.246). The distance of this from a sulphur atom was approximately 2.5 Å, so the peak could have been a nitrogen atom.

A second round of structure factor calculations reduced R to 0.244, and the missing light atoms were sought on a difference Fourier synthesis. Several peaks appeared, but some were obviously caused by diffraction ripples, and the N-C-N grouping could still not be unambiguously located.

A third round of structure factor calculations gave R = 0.241, and since this was scarcely any improvement on the previous value, least squares refinement was started using the eight known atomic positions.

Refinement. At the start of the refinement, R was 0.241. The following simple weighting scheme available on the Rollett structure factor least squares programme (S.F.L.S.) for DEUCE, was employed:

$\sqrt{w} = 1$ if $|F| \leq 12$, $\sqrt{w} = 12/|F|$ if $|F| > 12$.

As mentioned earlier, this programme had no facility for maintaining selected parameters constant, and all the atoms were allowedto vary. Two cycles of anisotropic, block-diagonal refinement reduced the R value to 0.185.

At this point, the DEUCE computer ceased to be available, and refinement was continued on the KDF - 9 computer, using the S.F.L.S. programme of D.W.J. Cruickshank and J.G.F. Smith. The weighting scheme was reconsidered. The data had been collected on a linear diffractometer, and it was not expected that there would be a great difference in the absolute error of measurement between high and low intensities in general, provided absorption and extinction effects were small. Accordingly, every reflection was initially weighted at unity. Since there were only eight atoms at this stage, anisotropic refinement was continued by full matrix least squares. There was, of course, only one overall scale factor. Two cycles reduced R to 0.160. A difference synthesis was computed, and revealed the remaining three atoms of the thiourea group. Inclusion of their co-ordinates, and temperature factors chosen to resemble those of the other light atoms, gave, an recalculation of the structure factors, an R factor of 0.152.

The following weighting scheme, suggested by D.W.J. Cruickshank, was found to be satisfactory:

$$\sqrt{w} = \frac{1 - \exp\left(-P_1 (\sin\theta/\lambda)^2\right)}{1 + P_2 |F| + P_3 |F|^2 + P_4 |F|^3}$$

In this analysis, $P_1 = 2.0$, $P_2 = P_3 = 0$, $P_4 = 2 \times 10^{-5}$

This had the effect of down weighting very strong reflections, and reflections affected by mis-setting at small sin θ.

One further cycle of S.F.L.S. refinement reduced R to 0.150. The final value of

$$R' = \sum w\Delta^2 \Big/ \sum w |F_o| k]^2$$

was 0.078 and $\sum w\Delta^2 = 17848.25$

3.2 Description of the Structure.

The structure of dibromobisthioureamercury (II) is similar to the structure of the corresponding chloro-compound, and it is convenient to describe the bromide with reference to the chloride.

The differences in cell dimensions are small

Chloride	Bromide
a = 12.79 Å	a = 13.03 Å
b = 5.89 Å	b = 6.19 Å
c = 6.44 Å	c = 6.31 Å
	γ = 90.3°

While the a-and b-axes have increased as would be expected, to accommodate the larger bromine atom, the c-axis has slightly decreased. As a consequence of this, the bonds in the approximately linear -Br-Hg-Br- chain parallel to the c-axis are shorter than these in the -Cl-Hg-Cl- chain. Also the bromine bridging bonds are unequal in length.

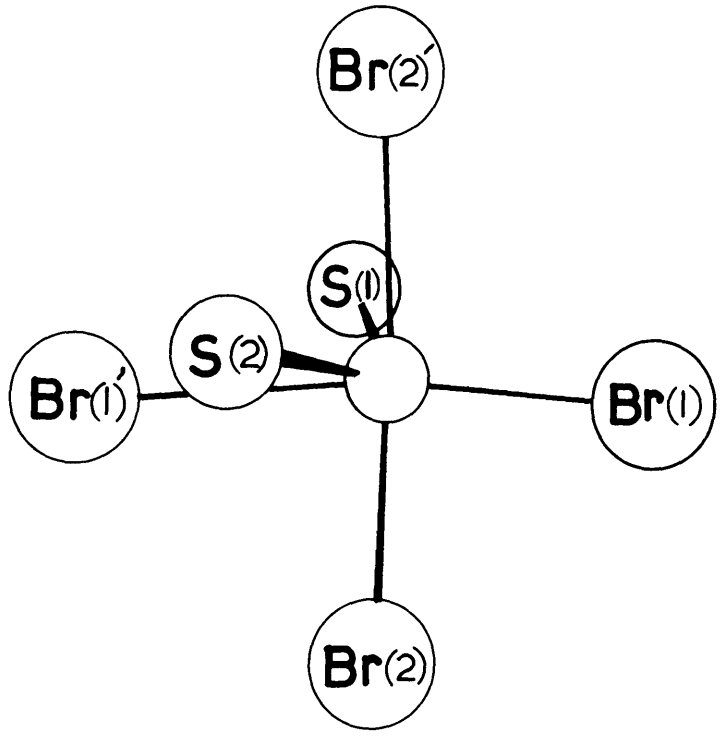
The $BrHgtu_2$ (tu = thiourea) group has been distorted relative to the $ClHgtu_2$ group, so that one thiourea lies out of the plane of the other atoms. The Br of a neighbouring $BrHgtu_2$ group is 3.41 Å from the mercury atom. Therefore the co-ordination of the mercury is most clearly pictured as very distorted octahedral.

Both independent Hg-S bonds are 2.42 Å long, and the S-Hg-S angle is 144.5°. All four bromine atoms are bridging, and the Hg-Br bond lengths range from 3.41 Å to 2.81 Å. The mercury co-ordination is described in detail in figure (6) and table (10 and (11). Figures (7) and (8) show the structure projected down the [001] and [010] axes. The arrangement of the co-ordination polyhedra is evident. The structure is, therefore, composed of sheets of distorted octahedra, linked through their comers, and lying normal to the a-axis. The repeat distance of the cell includes two sheets related by the 2_1 axis. A projection down [100] shows one such sheet: Figure (9). The sheets are 6.52 Å apart, and this space is occupied by the organic residue.

A major difference between the two structures is that, while in the chloro-compound, both thiourea groups lie normal to the c-axis, in the bromo-compound one lies normal to the c-axis, and the other is almost normal to the b-axis. In each group, the nitrogen atoms are positioned suitably for hydrogen bonding to bromine atoms. The bromines involved, are those bonded most closely to the mercury. The projections of the structure down [010] and [001] are remarkably similar.

Possible hydrogen bonds are indicated by dashed lines on figures (7) and (8).

Figure 6.



The immediate environment

of the mercury atom

Figure 7.

DIBROMOBISTHIOUREAMERCURY (II). Projection of the structure down the $\underline{c}$-axis. Possible hydrogen bonding is indicated by dashed lines.

Figure 7.

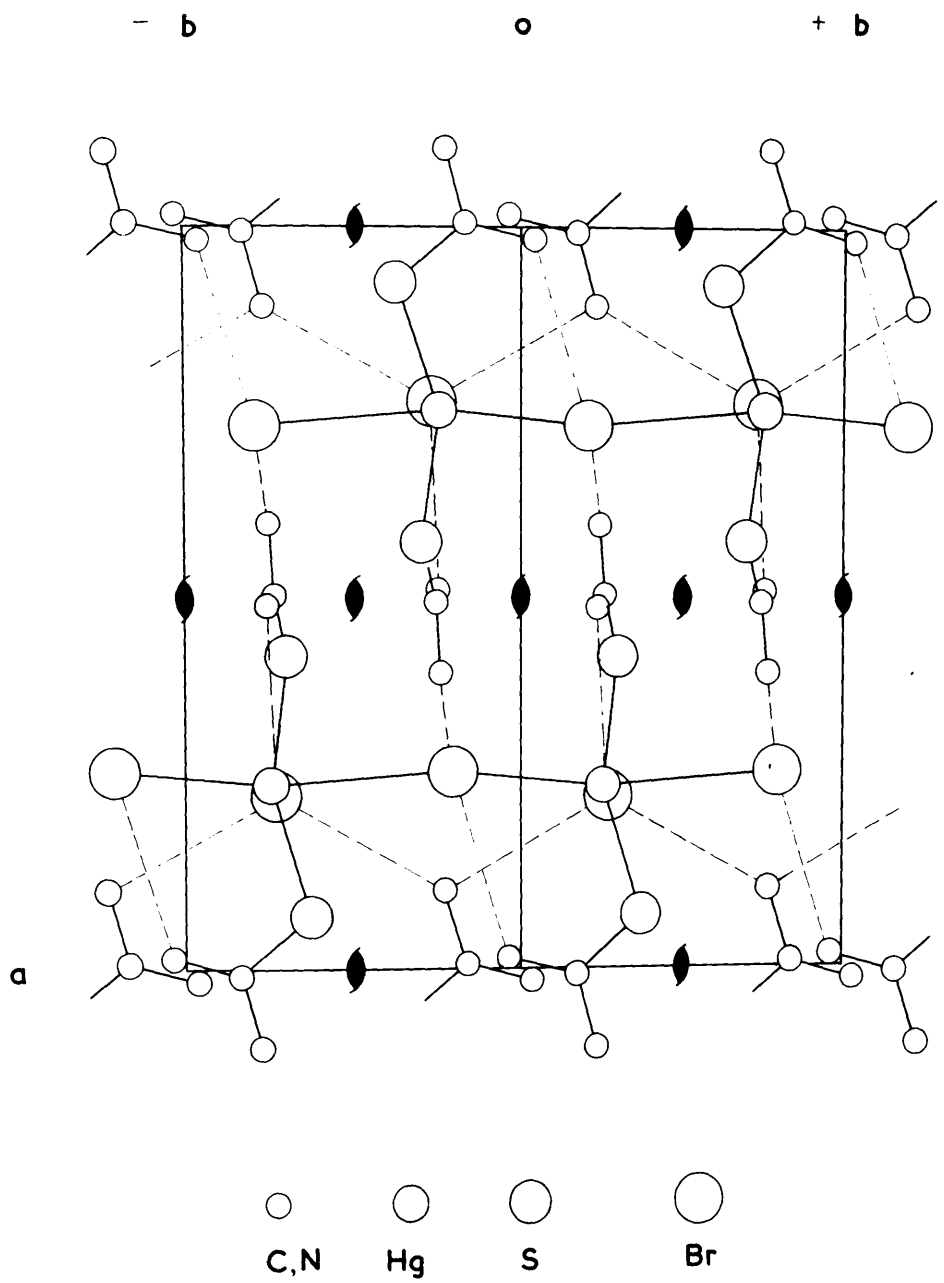


Figure 8.

DIBROMOBISTHIOUREAMERCURY (II). Projection of the structure down the b-axis. Possible hydrogen bonding is indicated by dashed lines.

Figure 8.

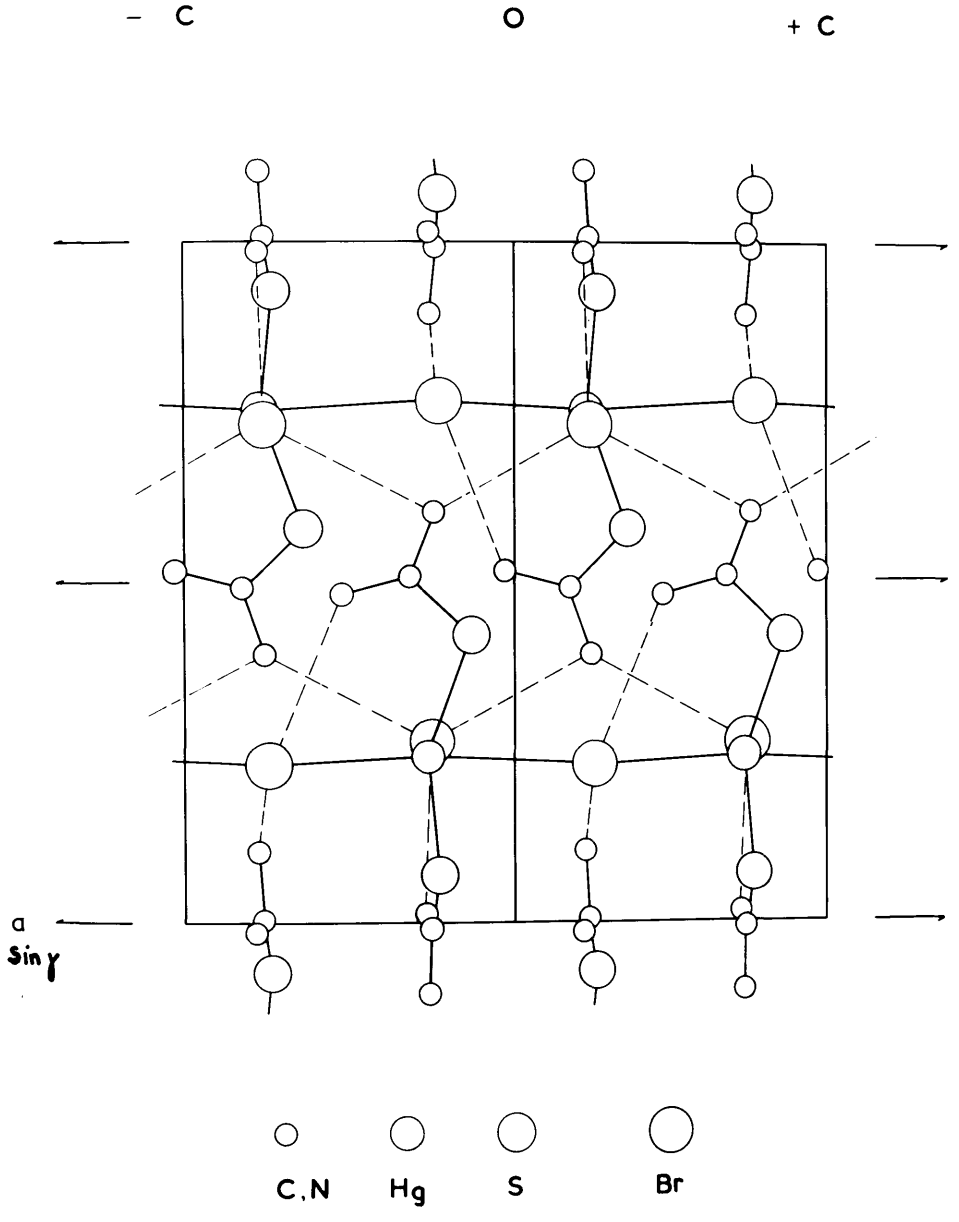


Figure 9.

DIBROMOBISTHIOUREAMERCURY (II). Projection down the $\underline{a}$-axis showing one sheet of mercury co-ordination polyhedra. The position of the mercury atom is marked by a cross.

Figure 9.

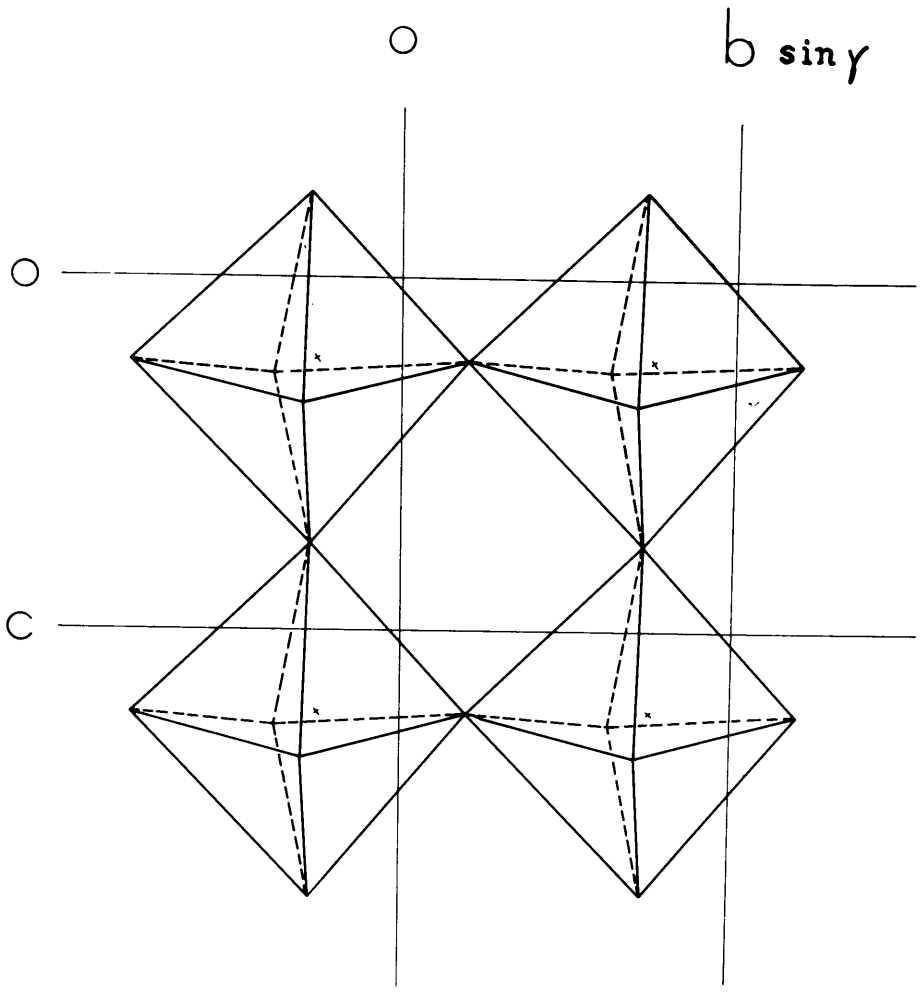


TABLE (7)

DIBROMOBISTHIOUREAMERCURY (II)

Fractional Atomic Co-ordinates

Atom	x	y	z
Hg	0.24705	-0.24929	0.23381
Br(1)	0.26866	0.20248	0.24352
Br(2)	0.23417	-0.26951	-0.24008
S (1)	0.07240	-0.37624	0.26738
S (2)	0.42120	-0.29420	0.36227
C (1)	-0.00677	-0.16563	0.23964
C (2)	0.50410	0.74556	0.15059
N (1)	-0.10590	-0.22361	0.22736
N (2)	0.01694	0.03701	0.22640
N (3)	0.60374	-0.24158	0.24375
N (4)	0.48100	-0.23300	-0.03000

TABLE (8)

DIBROMOBISTHIOUREAMERCURY (II)

Estimated Standard Deviations of the Fractional Atomic Co-ordinates

Atom	(x)	(y)	(z)
Hg	0.00012	0.00026	0.00000
Br(1)	0.00049	0.00106	0.00156
Br(2)	0.00077	0.00142	0.00285
S (1)	0.00150	0.00351	0.00849
S (2)	0.00104	0.00249	0.00276
C (1)	0.00266	0.00659	0.00780
C (2)	0.00315	0.00707	0.00740
N (1)	0.00264	0.00901	0.00658
N (2)	0.00396	0.00681	0.00797
N (3)	0.00365	0.00668	0.00844
N (4)	0.00409	0.00723	0.00786

TABLE (9)

DIBROMOBISTHIOUREAMERCURY (II)

Anisotropic Thermal Parameters ($Å^2$)

Atom	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Hg	0.0151	0.0242	0.0379	-0.0059	-0.0006	-0.0072
Br(1)	0.0216	0.0095	0.0649	-0.0140	-0.0000	-0.0154
Br(2)	0.0209	0.0244	0.1005	-0.0172	-0.0328	-0.0068
S (1)	0.0117	0.0170	0.1836	0.0179	-0.0012	-0.0093
S (2)	0.0151	0.0258	0.0375	0.0100	0.0004	-0.0014
C (1)	0.0073	0.0205	0.0179	-0.0421	0.0252	-0.0340
C (2)	0.0073	0.0205	0.0179	-0.0421	0.0252	-0.0340
N (1)	0.0014	0.0688	0.0134	0.0364	0.0258	-0.0503
N (2)	0.0296	0.0149	0.0234	0.0209	0.0013	-0.0217
N (3)	0.0296	0.0149	0.0234	0.0209	0.0013	-0.0217
N (4)	0.0296	0.0149	0.0234	0.0209	0.0013	-0.0217

TABLE (10)

DIBROMOBISTHIOUREAMERCURY (II)

Interatomic Bond Lengths in Å with Estimated Standard Deviations

Bond	Length	E.s.d
Hg - Br(1)	2.814	(0.008)
Hg - Br(1)'	3.413	(0.008)
Hg - Br(2)	2.998	(0.012)
Hg - Br(2)'	3.326	(0.012)
Hg - S (1)	2.415	(0.037)
Hg - S (2)	2.429	(0.015)
S(1) - C (1)	1.68	(0.06)
S(2) - C (2)	1.74	(0.05)
C(1) - N (1)	1.34	(0.06)
C(1) - N (2)	1.30	(0.06)
C(2) - N (3)	1.43	(0.06)
C(2) - N (4)	1.19	(0.06)
N(1) - Br(2)	3.50	
N(1) - Br(2)'	3.56	
N(2) - Br(1)	3.44	
N(2) - Br(2)	3.59	
N(3) - Br(1)	3.57	
N(3) - Br(1)'	3.57	
N(4) - Br(1)	3.57	
N(4) - Br(2)	3.49	

TABLE (11)

DIBROMOBISTHIOUREAMERCURY (II)

Inter-bond Angles with Estimated Standard Deviations

Atoms			Angle	E.s.d
Br(1)	- Hg	- Br(2)	93.9°	(0.3°)
Br(1)	- Hg	- Br(2)'	91.2°	(0.3°)
Br(1)	- Hg	- Br(1)'	169.3°	(0.3°)
Br(2)	- Hg	- Br(2)'	172.4°	(0.3°)
Br(2)	- Hg	- Br(1)'	88.9°	(0.3°)
Br(2)'	- Hg	- Br(1)'	87.1°	(0.3°)
S (1)	- Hg	- S (2)	144.5°	(1.0°)
S (1)	- Hg	- Br(1)	114.3°	(0.9°)
S (1)	- Hg	- Br(2)	91.2°	(0.9°)
S (1)	- Hg	- Br(2)'	81.5°	(0.9°)
S (1)	- Hg	- Br(1)'	75.9°	(0.9°)
S (2)	- Hg	- Br(1)	91.0°	(0.9°)
S (2)	- Hg	- Br(1)'	78.3°	(0.9°)
S (2)	- Hg	- Br(2)	112.4°	(0.9°)
S (2)	- Hg	- Br(2)'	73.1°	(0.9°)
N (1)	- C(1)	- N (2)	118.7°	(4.3°)
N (2)	- C(1)	- S (1)	128.1°	(3.6°)
N (1)	- C(1)	- S (1)	113.2°	(3.5°)
N (3)	- C(2)	- S (2)	104.9°	(3.6°)
N (4)	- C(2)	- S (2)	126.7°	(3.7°)
N (3)	- C(2)	- N (4)	128.4°	(4.4°)

TABLE (11) (contd)

Atoms	Angle
C (1) - N(2) - Br(2)	99.9°
C (1) - N(2) - Br(1)	120.7°
C (1) - N(1) - Br(2)'	103.1°
C (1) - N(1) - Br(2)''	132.9°
C (2) - N(4) - Br(2)	126.4°
C (2) - N(4) - Br(1)	99.1°
C (2) - N(3) - Br(1)	142.2°
C (2) - N(3) - Br(1)'	93.6°

TABLE (I2)

H	K	L	Fo	Fc
2	0	0	94.0	85.6
4	0	0	81.6	90.5
6	0	0	74.1	74.3
8	0	0	86.6	82.3
10	0	0	43.0	42.9
12	0	0	97.0	90.1
14	0	0	49.6	45.9
16	0	0	83.7	93.5
1	1	0	70.2	64.7
3	1	0	70.6	64.2
5	1	0	66.3	55.9
7	1	0	37.3	28.4
9	1	0	41.3	30.1
11	1	0	85.4	91.3
13	1	0	44.0	36.3
15	1	0	45.5	46.8
1	2	0	113.2	111.0
3	2	0	113.6	101.9
5	2	0	27.2	24.1
7	2	0	41.1	40.0
9	2	0	20.2	15.8
11	2	0	19.1	17.3
13	2	0	37.6	32.3
15	2	0	41.5	33.9
0	3	0	40.3	31.8
2	3	0	59.3	46.4
4	3	0	13.2	14.8
6	3	0	72.0	70.2
8	3	0	49.5	53.6
10	3	0	25.6	33.4
12	3	0	35.2	34.7
14	3	0	83.3	79.5
1	4	0	31.7	30.5
3	4	0	66.5	63.5
5	4	0	73.1	64.8
7	4	0	18.7	27.5
9	4	0	42.6	44.0
11	4	0	69.4	58.8
13	4	0	65.3	70.0
15	4	0	48.1	47.8
0	5	0	32.8	32.5
2	5	0	46.3	48.8
4	5	0	10.5	7.4
6	5	0	96.4	86.6
8	5	0	34.2	30.1
10	5	0	15.4	15.6
12	5	0	8.3	13.4
14	5	0	28.1	26.1
1	6	0	19.3	14.9
3	6	0	6.0	4.4
5	6	0	8.9	2.8
7	6	0	13.3	11.4
9	6	0	28.7	29.4
11	6	0	22.0	22.5
13	6	0	28.1	26.2
15	6	0	47.0	43.9
0	7	0	25.1	20.1
2	7	0	28.8	30.1
4	7	0	33.2	32.1
6	7	0	19.2	16.4
8	7	0	42.7	41.2
10	7	0	55.8	60.6
12	7	0	41.6	44.6
14	7	0	53.8	62.7
1	8	0	34.0	35.5
3	8	0	47.8	48.7
5	8	0	21.5	22.3
7	8	0	19.0	18.3
9	8	0	66.9	157.4
11	8	0	95.3	121.1
13	8	0	45.4	46.2
15	8	0	135.1	150.5
0	9	0	35.6	32.0
2	9	0	100.3	96.5
4	9	0	51.1	50.7
6	9	0	79.7	74.1
8	9	0	87.3	84.6
10	9	0	112.8	97.7
12	9	0	36.9	29.3
14	9	0	69.4	53.4
1	10	0	30.6	26.8
3	10	0	50.4	38.9
5	10	0	9.0	12.4
7	10	0	57.6	45.9
9	10	0	11.0	12.3
11	10	0	72.6	65.0
13	10	0	27.8	28.0
15	10	0	53.4	44.8
0	11	0	13.3	5.5
2	11	0	41.4	46.3
4	11	0	4.6	23.0
6	11	0	74.5	65.2
8	11	0	3.4	20.5
10	11	0	27.3	38.3
12	11	0	47.5	41.2
14	11	0	27.8	19.5
1	12	0	19.7	13.7
3	12	0	113.3	98.7
5	12	0	17.0	16.0
7	12	0	11.0	12.5
9	12	0	58.5	51.3
11	12	0	18.0	32.1
13	12	0	22.0	26.9
15	12	0	74.5	76.1
0	13	0	17.2	30.1
2	13	0	57.2	60.6
4	13	0	34.4	35.7
6	13	0	84.3	84.2
8	13	0	14.6	18.3
10	13	0	91.6	82.4
12	13	0	23.9	19.4
14	13	0	60.2	47.4
1	14	0	16.3	15.4
3	14	0	33.3	25.4
5	14	0	14.6	9.0
7	14	0	42.8	36.9
9	14	0	34.8	35.3
11	14	0	65.8	59.2
13	14	0	32.9	29.6
15	14	0	46.0	41.6
0	15	0	27.2	29.1
2	15	0	86.0	77.6
4	15	0	73.1	64.7
6	15	0	86.7	81.9
8	-2	1	22.5	20.3
3	-2	1	98.8	106.9
2	-2	1	28.6	27.2
1	-2	1	122.1	119.0
0	2	1	53.8	48.7
4	2	1	140.6	115.4
6	2	1	39.7	29.9
3	2	1	178.7	140.3
5	2	1	8.7	6.9
7	2	1	70.6	64.2
9	2	1	11.2	8.1
8	2	1	124.3	103.3
10	2	1	58.3	55.8
9	2	1	113.7	107.0
11	2	1	24.2	22.2
10	2	1	105.5	108.6
12	2	1	13.4	18.5
13	2	1	71.6	65.7
14	2	1	33.8	39.9
15	2	1	72.1	65.7
16	2	1	5.5	11.0
14	3	1	47.5	47.4
13	3	1	5.3	9.3
12	3	1	48.8	45.4
11	3	1	16.9	13.3
10	3	1	36.1	24.0
9	3	1	67.4	53.7
8	3	1	40.4	37.8
7	3	1	37.4	28.8
6	3	1	8.2	16.1
5	3	1	56.2	44.0
4	3	1	94.5	71.4
3	3	1	32.7	23.9
2	3	1	69.9	58.0
1	3	1	57.7	57.7
1	-3	1	25.9	23.3
2	-3	1	44.6	44.1
3	-3	1	79.6	76.4
4	-3	1	42.3	46.8
5	-3	1	36.9	43.0
6	-3	1	59.3	60.0
7	-3	1	14.9	24.0
8	-3	1	68.6	67.4
9	-3	1	36.8	40.4
10	-3	1	56.2	58.3
11	-3	1	17.8	18.6
12	-3	1	59.8	58.1
13	-3	1	3.5	7.6
14	-3	1	60.5	55.6
15	-3	1	16.9	17.5
14	-4	1	23.8	22.7
13	-4	1	25.8	24.0
12	-4	1	6.6	4.3
11	-4	1	31.9	32.4
10	-4	1	23.9	19.0
9	-4	1	23.8	26.8
8	-4	1	37.8	37.1
7	-4	1	44.1	39.6
6	-4	1	11.6	7.6
5	-4	1	77.1	75.8
4	-4	1	38.5	36.7
3	-4	1	51.1	46.9
2	-4	1	53.8	62.7
1	4	1	108.8	90.8
1	-4	1	4.4	14.0
2	-4	1	122.4	100.4
3	-4	1	12.9	12.1
4	-4	1	109.4	93.3
5	-4	1	7.0	6.2
6	-4	1	113.6	95.0
7	-4	1	34.1	30.7
8	-4	1	120.7	110.4
9	-4	1	10.5	10.0
10	-4	1	79.6	76.4
11	-4	1	20.6	21.4
12	-4	1	61.1	66.9
13	-4	1	34.4	34.9
14	-4	1	11.7	9.0
15	-4	1	20.8	15.5
16	-4	1	27.2	29.6
15	-5	1	54.7	46.1
14	-5	1	37.4	33.5
13	-5	1	47.5	48.7
12	-5	1	54.7	49.1
11	-5	1	26.2	23.4
10	-5	1	52.5	47.0
9	-5	1	69.9	64.3
8	-5	1	75.6	70.4
7	-5	1	44.3	44.0
6	-5	1	38.9	32.3
5	-5	1	46.0	46.7
4	-5	1	55.5	53.4
3	-5	1	63.5	63.4
2	-5	1	38.0	38.4
1	-5	1	47.2	49.8
1	5	1	19.5	20.6
2	5	1	52.0	52.4
3	5	1	15.2	17.1
4	5	1	58.6	57.1
5	5	1	17.1	16.5
6	5	1	37.3	36.0
7	5	1	7.2	3.4
8	5	1	9.9	9.4
9	5	1	6.9	2.7
10	5	1	24.6	27.2
11	5	1	15.9	14.0
12	5	1	22.9	25.8
13	5	1	11.7	8.5
14	5	1	18.3	23.0
15	5	1	5.8	12.3
16	5	1	5.0	5.1
15	6	1	11.8	17.1
14	6	1	57.2	56.3
13	6	1	19.5	15.6
12	6	1	51.6	49.1
11	6	1	10.4	4.8
10	6	1	79.5	79.0
9	6	1	62.8	65.1
8	6	1	42.2	45.2
7	6	1	40.5	45.4
6	6	1	31.3	33.2
5	6	1	35.4	42.9
4	6	1	42.9	49.5
3	6	1	32.2	33.1
2	6	1	47.2	56.5
1	6	1	30.9	37.8
0	6	1	32.6	35.6
1	-6	1	27.7	25.7
2	-6	1	51.1	54.0
3	-6	1	14.4	16.9
4	-6	1	81.1	83.2
5	-6	1	131.0	108.5
6	-6	1	19.5	19.8
7	-6	1	151.4	187.8
8	-6	1	6.9	23.4
9	-6	1	161.9	179.4
10	-6	1	11.6	9.7
11	-6	1	135.4	137.2
12	-6	1	100.2	94.1
13	-6	1	96.0	88.7
14	-6	1	22.0	19.6
15	-6	1	59.8	55.4
16	-6	1	16.3	17.5
0	1	2	154.8	117.9
1	1	2	42.0	30.9
2	1	2	139.3	114.1
3	1	2	18.5	24.7
4	1	2	129.1	116.7
5	1	2	76.7	70.0
6	1	2	71.4	70.6
7	1	2	47.3	45.7
8	1	2	70.6	80.5
9	1	2	57.8	61.0
10	1	2	84.2	83.2
11	1	2	68.0	65.3
12	1	2	46.4	44.5
13	1	2	46.7	47.0
14	1	2	55.3	54.7
15	1	2	38.5	37.7
0	-1	2	139.5	143.0
1	-1	2	51.6	51.6
2	-1	2	107.3	107.1
3	-1	2	52.9	52.1
4	-1	2	108.7	116.4
5	-1	2	72.6	72.9
6	-1	2	74.0	81.1
7	-1	2	52.8	53.1
8	-1	2	104.8	99.8
9	-1	2	52.7	54.7
10	-1	2	74.6	69.6
11	-1	2	59.3	50.8
0	2	2	235.4	197.5
1	2	2	63.2	64.0
2	2	2	235.1	182.8
3	2	2	28.4	18.3
4	2	2	231.4	174.8
5	2	2	58.2	56.6
6	2	2	194.4	163.6
7	2	2	31.1	26.2
8	2	2	143.3	134.0
9	2	2	19.6	19.3
10	2	2	105.5	106.3
11	2	2	29.3	27.5
12	2	2	75.6	83.9
13	2	2	13.7	15.0
14	2	2	66.3	69.5
15	2	2	6.5	10.2
1	-2	2	49.9	47.1
2	-2	2	170.6	195.4
3	-2	2	6.4	11.1
4	-2	2	128.2	130.2
5	-2	2	29.8	27.2
6	-2	2	147.9	140.8
7	-2	2	4.9	16.7
8	-2	2	118.4	112.3
9	-2	2	1.1	17.7
10	-2	2	79.9	77.5
11	-2	2	6.2	4.2
12	-2	2	66.9	66.3
13	-2	2	14.4	17.1
14	-2	2	57.4	51.6
15	-2	2	27.2	22.0
16	-2	2	14.0	21.8
1	3	2	109.0	89.9
2	3	2	14.4	17.1
3	3	2	135.5	107.0
4	3	2	22.5	21.5
5	3	2	89.6	75.6
6	3	2	37.6	35.0
7	3	2	84.7	88.3
8	3	2	16.1	20.4
9	3	2	67.4	68.4
10	3	2	56.6	57.7
11	3	2	26.1	38.8
12	3	2	28.4	38.4
13	3	2	30.3	30.9
14	3	2	112.9	108.2
15	3	2	40.4	38.8
1	-3	2	130.7	130.5
2	-3	2	47.6	47.4
3	-3	2	97.4	102.3
4	-3	2	46.7	46.0
5	-3	2	109.8	108.1
6	-3	2	52.2	47.3
7	-3	2	122.3	94.8
8	-3	2	58.9	50.4
9	-3	2	32.6	29.2
10	-3	2	71.5	70.1
11	-3	2	35.1	37.0
12	-3	2	27.2	17.9
13	-3	2	50.5	43.6
14	-3	2	53.1	53.5
15	-3	2	58.6	45.0
16	-3	2	40.9	41.8
1	4	2	64.6	58.1
2	4	2	140.9	118.8
3	4	2	68.6	61.3
4	4	2	126.3	117.6
5	4	2	38.4	35.8
6	4	2	118.8	112.0
7	4	2	32.7	37.2
8	4	2	86.4	85.6
9	4	2	25.5	30.7
10	4	2	63.0	70.8
11	4	2	8.4	14.4
12	4	2	58.1	53.8
13	4	2	121.0	117.6
14	4	2	31.4	31.7
2	7	1	42.9	49.5
1	7	1	32.2	33.1
0	7	1	47.2	56.5
1	-7	1	30.9	37.8
2	-7	1	32.6	35.6
3	-7	1	27.7	25.7
4	-7	1	51.1	54.0
5	-7	1	14.4	16.9
6	-7	1	81.1	83.2
2	0	0	131.0	108.5
3	0	0	19.5	19.8
4	0	0	151.4	187.8
5	0	0	6.9	23.4
6	0	0	161.9	179.4
7	0	0	11.6	9.7
8	0	0	135.4	137.2
9	0	0	100.2	94.1
10	0	0	96.0	88.7
11	0	0	22.0	19.6
12	0	0	59.8	55.4
13	0	0	16.3	17.5
0	1	1	47.5	47.4
1	1	1	5.3	9.3
2	1	1	48.8	45.4
3	1	1	16.9	13.3
4	1	1	36.1	24.0
5	1	1	67.4	53.7
6	1	1	40.4	37.8
7	1	1	37.4	28.8
8	1	1	8.2	16.1
9	1	1	56.2	44.0
10	1	1	94.5	71.4
11	1	1	32.7	23.9
12	1	1	69.9	58.0
13	1	1	57.7	57.7
14	1	1	25.9	23.3
15	1	1	44.6	44.1
0	-1	1	79.6	76.4
1	-1	1	42.3	46.8
2	-1	1	36.9	43.0
3	-1	1	59.3	60.0
4	-1	1	14.9	24.0
5	-1	1	68.6	67.4
6	-1	1	36.8	40.4
7	-1	1	56.2	58.3
8	-1	1	17.8	18.6
9	-1	1	59.8	58.1
10	-1	1	3.5	7.6
11	-1	1	60.5	55.6
12	-1	1	16.9	17.5
13	-1	1	23.8	22.7
14	-1	1	25.8	24.0
15	-1	1	6.6	4.3
0	2	1	31.9	32.4
1	2	1	23.9	19.0
2	2	1	23.8	26.8
3	2	1	37.8	37.1
4	2	1	44.1	39.6
5	2	1	11.6	7.6
6	2	1	77.1	75.8
7	2	1	38.5	36.7
8	2	1	51.1	46.9
9	2	1	53.8	62.7
10	2	1	108.8	90.8
11	2	1	4.4	14.0
12	2	1	122.4	100.4
13	2	1	12.9	12.1
14	2	1	109.4	93.3
15	2	1	7.0	6.2
16	2	1	113.6	95.0
15	3	1	34.1	30.7
14	3	1	120.7	110.4
13	3	1	10.5	10.0
12	3	1	79.6	76.4
11	3	1	20.6	21.4
10	3	1	61.1	66.9
9	3	1	34.4	34.9
8	3	1	11.7	9.0
7	3	1	20.8	15.5
6	3	1	27.2	29.6
5	3	1	54.7	46.1
4	3	1	37.4	33.5
3	3	1	47.5	48.7
2	3	1	54.7	49.1
1	3	1	26.2	23.4
0	3	1	52.5	47.0
1	-3	1	69.9	64.3
2	-3	1	75.6	70.4
3	-3	1	44.3	44.0
4	-3	1	38.9	32.3
5	-3	1	46.0	46.7
6	-3	1	55.5	53.4
7	-3	1	63.5	63.4
8	-3	1	38.0	38.4
9	-3	1	47.2	49.8
10	-3	1	19.5	20.6
11	-3	1	52.0	52.4
12	-3	1	15.2	17.1
13	-3	1	58.6	57.1
14	-3	1	17.1	16.5
15	-3	1	37.3	36.0
16	-3	1	7.2	3.4
15	-4	1	9.9	9.4
14	-4	1	6.9	2.7
13	-4	1	24.6	27.2
12	-4	1	15.9	14.0
11	-4	1	22.9	25.8
10	-4	1	11.7	8.5
9	-4	1	18.3	23.0
8	-4	1	5.8	12.3
7	-4	1	5.0	5.1
6	-4	1	11.8	17.1
5	-4	1	57.2	56.3
4	-4	1	19.5	15.6
3	-4	1	51.6	49.1
2	-4	1	10.4	4.8
1	-4	1	79.5	79.0
0	4	1	62.8	65.1
1	4	1	42.2	45.2
2	4	1	40.5	45.4
3	4	1	31.3	33.2
4	4	1	35.4	42.9
5	4	1	42.9	49.5
6	4	1	32.2	33.1
7	4	1	47.2	56.5
8	4	1	30.9	37.8
9	4	1	32.6	35.6
10	4	1	27.7	25.7
11	4	1	51.1	54.0
12	4	1	14.4	16.9
13	4	1	81.1	83.2
14	4	1	131.0	108.5
15	4	1	19.5	19.8
16	4	1	151.4	187.8
15	5	1	6.9	23.4
14	5	1	161.9	179.4
13	5	1	11.6	9.7
12	5	1	135.4	137.2
11	5	1	100.2	94.1
10	5	1	96.0	88.7
9	5	1	22.0	19.6
8	5	1	59.8	55.4
7	5	1	16.3	17.5
6	5	1	154.8	117.9
5	5	1	42.0	30.9
4	5	1	139.3	114.1
3	5	1	18.5	24.7
2	5	1	129.1	116.7
1	5	1	76.7	70.0
0	5	1	71.4	70.6
1	-5	1	47.3	45.7
2	-5	1	70.6	80.5
3	-5	1	57.8	61.0
4	-5	1	84.2	83.2
5	-5	1	68.0	65.3
6	-5	1	46.4	44.5
7	-5	1	46.7	47.0
8	-5	1	55.3	54.7
9	-5	1	38.5	37.7
10	-5	1	139.5	143.0
11	-5	1	51.6	51.6
12	-5	1	107.3	107.1
13	-5	1	52.9	52.1
14	-5	1	108.7	116.4
15	-5	1	72.6	72.9
16	-5	1	74.0	81.1
15	-6	1	52.8	53.1
14	-6	1	104.8	99.8
13	-6	1	52.7	54.7
12	-6	1	74.6	69.6
11	-6	1	59.3	50.8
0	6	1	61.7	63.0
1	6	1	36.4	38.6
2	6	1	73.6	75.9
3	6	1	48.1	48.4
4	6	1	56.9	59.0
5	6	1	54.9	53.0
6	6	1	69.7	77.7
7	6	1	40.5	45.4
8	6	1	64.6	67.9
9	6	1	35.9	39.0
10	6	1	30.2	34.3
11	6	1	53.1	56.1
12	6	1	24.5	26.0
13	6	1	52.0	52.2
14	6	1	7.8	11.1
15	6	1	37.8	46.5
14	7	1	3.5	4.6
13	7	1	34.4	34.9
12	7	1	13.3	6.6
11	7	1	35.4	38.1
10	7	1	19.7	17.7
9	7	1	25.6	24.1
8	7	1	3.6	3.6
7	7	1	59.7	66.1
6	7	1	3.6	8.3
5	7	1	43.1	49.9
4	7	1	3.7	10.7
3	7	1	37.7	47.7
2	7	1	10.1	12.2
1	7	1	25.2	34.2
0	7	1	3.9	3.6
1	-7	1	16.7	24.4
2	-7	1	56.2	62.2
3	-7	1	28.1	30.3
4	-7	1	13.8	28.3
5	-7	1	15.3	9.4
6	-7	1	17.6	9.4
7	-7	1	53.8	47.3
8	-7	1	17.0	17.2
9	-7	1	39.8	39.8
10	-7	1	49.2	46.9
11	-7	1	64.9	57.5
12	-7	1	64.9	51.7
13	-7	1	52.9	54.8
14	-7	1	35.4	36.6
15	-7	1	33.5	38.8
14	-8	1	27.6	36.8
13	-8	1	61.9	56.4
12	-8	1	37.0	39.7
11	-8	1	21.8	24.6
10	-8	1	39.4	47.0
9	-8	1	24.1	27.6
8	-8	1	22.3	33.4
7	-8	1	15.2	17.5
6	-8	1	13.8	10.2
5	-8	1	19.1	9.2
4	-8	1	3.3	14.5
3	-8	1	14.1	20.7
2	-8	1	9.2	9.8
1	-8	1	13.8	21.6
0	-8	1	8.9	5.5
1	8	1	42.4	40.4
2	8	1	3.4	9.9
3	8	1	50.0	50.7
4	8	1	17.0	23.5
5	8	1	42.8	45.4
6	8	1	29.1	29.8
7	8	1	40.3	41.1
8	8	1	27.4	29.4
9	8	1	52.4	56.7
10	8	1

TABLE (I2) (CONTD.)

H	K	L	Fo	Fc
2	8	3	4.0	10.4
1	8	3	13.2	15.2
0	8	3	12.6	2.8
1	-8	3	12.6	16.1
3	7	3	13.3	24.2
4	7	3	28.0	34.0
5	7	3	29.7	30.3
6	7	3	27.8	36.2
7	7	3	13.6	19.4
8	7	3	17.0	23.1
9	-6	3	18.0	15.7
10	-6	3	9.4	4.5
11	-6	3	16.8	12.5
12	-6	3	18.2	8.4
12	-5	3	34.9	33.7
11	-5	3	10.5	18.1
12	5	3	6.7	22.4
13	5	3	4.0	1.5
13	4	3	26.5	59.5
12	4	3	15.0	15.5
12	-4	3	8.8	9.8
13	-4	3	25.4	23.7
14	-4	3	3.9	5.3
15	-4	3	20.2	19.0
16	-4	3	8.7	8.4
16	-3	3	55.5	53.9
13	-3	3	3.5	14.4
13	3	3	6.3	13.4
14	3	3	16.9	19.6
15	3	3	11.8	14.9
16	3	3	8.1	35.6
16	2	3	3.9	13.2
15	2	3	21.5	56.2
15	-2	3	29.2	30.4
14	-2	3	12.4	6.4
17	-2	3	16.4	19.8
17	-1	3	11.4	10.7
16	-1	3	40.3	41.2
17	1	3	7.0	15.6
17	0	3	15.0	35.9
16	0	3	11.6	16.9
1	0	4	90.8	105.2
1	0	4	12.8	21.7
2	0	4	96.3	120.1
3	0	4	5.8	8.5
4	0	4	114.8	122.7
5	0	4	5.1	9.9
6	0	4	91.2	94.8
7	0	4	9.5	5.2
8	0	4	101.5	100.8
9	0	4	7.2	7.0
10	0	4	75.0	66.3
11	0	4	6.5	10.1
12	0	4	56.4	52.8
13	0	4	18.9	20.0
14	0	4	52.3	58.5
1	1	4	89.6	65.0
2	1	4	30.0	23.8
3	1	4	102.3	83.8
4	1	4	3.7	6.5
5	1	4	75.4	70.8
6	1	4	30.1	29.6
7	1	4	41.8	42.5
8	1	4	39.0	39.0
9	1	4	66.3	71.8
10	1	4	22.0	25.9
11	1	4	47.7	50.9
12	1	4	36.9	39.5
13	1	4	42.0	38.6
14	1	4	34.7	32.0
1	-1	4	58.7	63.6
2	-1	4	19.7	22.1
3	-1	4	97.4	97.9
4	-1	4	22.2	20.7
5	-1	4	61.9	62.8
6	-1	4	30.8	30.0
7	-1	4	65.2	68.1
8	-1	4	46.6	48.9
9	-1	4	67.4	70.5
10	-1	4	16.7	19.2
11	-1	4	58.7	58.0
12	-1	4	42.5	40.9
13	-1	4	36.3	40.6
14	-1	4	30.4	28.5
15	-1	4	55.6	46.8
0	2	4	130.2	112.7
1	2	4	31.7	27.2
2	2	4	185.9	110.4
3	2	4	28.3	19.5
4	2	4	153.7	117.9
5	2	4	9.1	20.8
6	2	4	111.4	95.5
7	2	4	19.1	21.2
8	2	4	103.1	94.9
9	2	4	2.9	16.7
10	2	4	78.2	75.3
11	2	4	12.0	6.2
12	2	4	53.9	56.6
13	2	4	14.1	19.1
14	2	4	14.4	18.2
1	-2	4	120.3	121.4
2	-2	4	14.7	15.9
3	-2	4	89.6	85.3
4	-2	4	22.8	17.9
5	-2	4	86.4	83.3
6	-2	4	7.2	5.4
7	-2	4	34.2	30.4
8	-2	4	7.0	8.3
9	-2	4	53.8	51.6
10	-2	4	7.1	2.2
11	-2	4	37.4	38.8
12	-2	4	14.8	14.4
13	-2	4	31.2	24.5
0	3	4	60.9	51.0
1	3	4	8.2	8.0
2	3	4	89.7	74.3
3	3	4	8.8	6.3
4	3	4	66.1	58.1
5	3	4	7.1	11.2
6	3	4	35.8	29.4
7	3	4	23.4	23.3
8	3	4	60.1	59.8
9	3	4	21.0	27.3
10	3	4	34.2	36.8
12	3	4	7.8	10.4
1	-3	4	77.8	70.3
2	-3	4	22.5	21.8
3	-3	4	81.6	83.1
4	-3	4	21.2	19.2
5	-3	4	60.5	63.3
6	-3	4	33.9	32.6
7	-3	4	68.3	68.5
8	-3	4	31.3	31.1
9	-3	4	72.1	69.3
10	-3	4	14.5	18.2
11	-3	4	46.1	49.7
12	-3	4	32.6	27.7
0	4	4	85.8	79.5
1	4	4	22.8	26.3
2	4	4	92.0	77.3
3	4	4	43.7	34.2
4	4	4	106.8	88.9
5	4	4	17.4	26.5
6	4	4	85.9	78.1
7	4	4	24.5	26.8
8	4	4	77.7	73.4
9	4	4	21.6	26.1
10	4	4	69.6	67.3
11	4	4	11.2	10.8
1	-4	4	19.9	22.0
2	-4	4	86.9	81.6
3	-4	4	27.7	26.7
4	-4	4	54.8	56.7
5	-4	4	2.8	6.4
6	-4	4	49.8	53.4
7	-4	4	4.2	7.6
8	-4	4	52.5	55.4
9	-4	4	4.6	5.4
10	-4	4	34.7	32.9
11	-4	4	7.0	7.3
0	5	4	27.3	27.6
1	5	4	30.7	28.5
2	5	4	50.1	48.5
3	5	4	10.4	8.1
4	5	4	58.5	58.1
5	5	4	8.8	6.4
6	5	4	50.5	47.2
7	5	4	14.9	10.9
8	5	4	19.2	25.8
9	5	4	10.9	12.5
10	5	4	30.8	38.6
11	5	4	11.6	15.1
12	5	4	59.9	59.1
2	-5	4	11.2	11.7
3	-5	4	68.3	66.5
4	-5	4	10.2	16.2
5	-5	4	54.5	54.1
6	-5	4	21.4	21.6
7	-5	4	58.4	59.2
8	-5	4	23.9	24.9
9	-5	4	53.0	52.3
10	-5	4	5.1	9.6
1	6	4	39.4	46.5
2	6	4	12.5	20.2
3	6	4	44.8	44.2
4	6	4	28.8	33.3
5	6	4	50.4	51.1
6	6	4	17.5	24.6
7	6	4	53.2	54.5
8	6	4	15.0	27.4
9	6	4	39.8	46.2
1	-6	4	13.7	19.7
2	-6	4	46.4	45.6
3	-6	4	16.2	19.8
4	-6	4	23.5	26.4
5	-6	4	6.0	2.6
6	-6	4	27.7	36.7
7	-6	4	8.8	3.5
8	-6	4	16.2	26.5
0	7	4	3.8	3.9
1	7	4	8.2	15.5
2	7	4	31.8	38.3
3	7	4	5.2	11.3
4	7	4	34.2	38.3
5	7	4	10.0	5.6
1	-7	4	41.7	50.1
2	-7	4	7.5	2.7
3	-7	4	40.9	33.8
4	-7	4	48.2	44.0
1	-1	5	20.6	22.3
2	-1	5	14.6	18.2
3	-1	5	51.9	54.1
4	-1	5	13.3	6.3
5	-1	5	45.5	40.6
6	-1	5	46.8	51.0
7	-1	5	5.4	16.5
8	-1	5	3.8	10.5
9	-1	5	35.9	34.1
10	-1	5	13.5	5.5
11	-1	5	25.2	28.7
12	-1	5	9.6	7.3
13	-1	5	23.2	18.6
14	-1	5	39.5	41.9
15	-1	5	28.3	22.2
16	-1	5	16.0	11.9
17	-1	5	34.4	38.8
0	8	4	7.8	12.2
1	8	4	9.9	24.5
2	8	4	10.7	11.9
3	8	4	38.4	68.6
4	8	4	3.3	7.1
5	8	4	73.2	53.6
6	8	4	10.8	19.6
7	8	4	61.7	64.4
8	8	4	4.9	7.8
7	0	5	58.7	50.5
8	0	5	4.4	6.3
9	0	5	65.1	55.6
10	0	5	7.8	16.6
11	0	5	45.6	42.7
0	1	5	39.7	45.8
1	1	5	5.9	10.7
2	1	5	45.2	38.6
3	1	5	6.6	6.7
4	1	5	37.3	40.7
5	1	5	11.0	12.4
6	1	5	38.2	37.4
7	1	5	19.9	17.9
8	1	5	39.9	42.1
9	1	5	45.7	47.0
10	1	5	19.6	21.0
11	1	5	38.1	33.5
12	1	5	15.0	11.6
13	1	5	36.7	32.7
0	2	5	8.0	2.6
1	2	5	84.8	61.1
2	2	5	20.8	14.5
3	2	5	110.7	79.8
4	2	5	3.7	8.1
5	2	5	84.0	64.1
6	2	5	2.4	6.3
7	2	5	67.6	50.8
8	2	5	7.8	2.4
9	2	5	65.6	60.5
10	2	5	6.2	7.5
11	2	5	49.9	49.4
12	2	5	4.8	9.4
1	-2	5	70.9	60.9
2	-2	5	9.0	8.0
3	-2	5	73.8	71.9
4	-2	5	18.1	20.9
5	-2	5	50.8	48.0
6	-2	5	5.9	11.6
7	-2	5	53.3	47.1
8	-2	5	9.5	6.7
9	-2	5	44.1	37.9
10	-2	5	11.0	17.0
11	-2	5	33.4	34.7
12	-2	5	4.8	6.3
0	3	5	42.4	40.7
1	3	5	8.5	5.8
2	3	5	45.5	32.9
3	3	5	13.8	16.2
4	3	5	47.6	33.5
5	3	5	9.7	6.3
6	3	5	35.6	32.0
7	3	5	7.5	21.9
8	3	5	34.9	30.5
9	3	5	20.5	13.2
10	3	5	31.8	25.3
1	-3	5	30.9	26.4
2	-3	5	51.5	48.0
3	-3	5	11.7	12.0
4	-3	5	36.0	33.0
5	-3	5	20.9	22.1
6	-3	5	44.8	44.3
7	-3	5	20.3	17.2
8	-3	5	46.1	42.9
9	-3	5	12.0	13.7
10	-3	5	35.6	33.1
11	-3	5	17.2	14.6
0	4	5	12.7	2.3
1	4	5	39.8	49.0
2	4	5	26.3	21.0
3	4	5	64.7	54.0
4	4	5	8.9	5.7
5	4	5	72.3	57.7
6	4	5	6.7	7.7
7	4	5	48.2	38.4
8	4	5	7.9	3.1
9	4	5	60.1	57.0
10	4	5	11.6	8.4
1	-4	5	49.2	41.5
2	-4	5	14.9	17.2
3	-4	5	49.5	48.8
4	-4	5	21.2	13.8
5	-4	5	33.3	33.1
6	-4	5	3.0	4.0
7	-4	5	36.0	32.4
8	-4	5	2.2	6.1
9	-4	5	28.2	25.2
0	5	5	30.8	30.0
1	5	5	8.0	18.9
2	5	5	35.7	34.6
3	5	5	6.2	12.1
4	5	5	26.8	21.3
5	5	5	21.7	19.1
6	5	5	36.9	34.6
7	5	5	8.3	11.5
8	5	5	11.0	15.5
1	-5	5	21.4	17.3
2	-5	5	49.1	45.2
3	-5	5	14.5	13.3
4	-5	5	31.8	28.1
5	-5	5	17.9	17.7
6	-5	5	45.5	41.5
7	-5	5	13.9	12.2
8	-5	5	35.7	32.6
9	-5	5	6.2	9.4
0	6	5	9.5	7.7
1	6	5	25.0	25.4
2	6	5	14.5	13.0
3	6	5	34.0	35.9
4	6	5	11.6	14.0
5	6	5	22.8	29.2
6	6	5	12.1	9.3
7	-6	5	15.4	22.5
8	-6	5	6.8	3.7
0	7	5	26.2	29.1
1	7	5	3.7	11.8
12	0	5	9.8	7.5
13	0	5	38.6	29.5
14	0	5	8.1	5.0
15	0	5	36.7	29.2
16	0	5	3.9	9.0
13	1	5	23.4	19.5
14	1	5	38.3	38.8
15	1	5	15.7	11.2
16	1	5	30.3	25.7
15	-1	5	24.1	20.4
14	-1	5	42.9	38.1
15	-1	5	8.5	9.2
13	2	5	33.2	26.2
14	2	5	39.0	30.6
14	2	5	9.9	3.1
15	2	5	38.9	35.3
16	2	5	4.0	6.9
15	-2	5	31.5	23.4
16	-2	5	7.0	6.4
11	3	5	5.9	9.6
12	3	5	18.2	25.1
13	3	5	14.4	15.3
14	3	5	24.1	28.0
15	3	5	13.3	9.4
16	3	5	24.6	20.9
12	-3	5	30.4	28.2
13	-3	5	14.7	11.4
14	-3	5	37.1	37.0
15	-3	5	5.6	9.2
11	4	5	47.0	42.1
12	4	5	3.7	9.2
13	4	5	35.0	33.6
14	4	5	12.4	21.9
12	-4	5	9.8	4.1
13	-4	5	12.2	18.6
14	-4	5	4.0	6.9
15	-4	5	17.5	14.3
9	5	5	3.6	1.7
10	5	5	26.7	24.7
11	5	5	6.7	10.9
12	5	5	15.9	15.5
13	5	5	4.1	5.4
10	-5	5	32.2	29.7
11	-5	5	11.4	10.7
5	6	5	40.9	34.5
6	6	5	3.6	2.6
7	6	5	38.4	32.0
8	6	5	14.7	17.0
8	-6	5	5.3	3.9
9	-6	5	13.5	15.5
10	-6	5	5.8	5.3
11	-6	5	4.0	13.4
7	7	5	15.5	25.8
8	7	5	14.7	14.2
9	7	5	19.6	20.4
10	7	5	8.7	9.1
6	8	5	28.8	28.4
7	7	5	12.1	12.6
7	-7	5	9.1	12.2
9	8	5	12.9	3.6
1	8	5	13.8	13.9
1	-8	5	4.1	13.1
2	8	5	35.3	61.3
4	8	6	43.8	55.4
5	8	6	40.0	58.1
6	8	6	10.1	11.9
7	8	6	44.4	49.7
8	8	6	35.2	36.6
0	1	6	5.6	7.2
1	1	6	39.7	42.2
2	1	6	37.4	41.9
3	1	6	7.0	4.2
4	1	6	27.0	31.0
5	1	6	27.1	31.8
6	1	6	8.5	15.9
7	1	6	28.9	36.7
8	1	6	9.6	15.8
9	1	6	27.5	36.8
10	1	6	21.0	34.0
2	-1	6	4.8	9.3
3	-1	6	37.0	49.8
4	-1	6	13.1	14.5
5	-1	6	25.7	37.7
6	-1	6	26.2	39.7
8	-1	6	10.4	19.1
9	-1	6	27.1	34.8
11	-1	6	37.7	40.9
0	2	6	58.2	57.9
1	2	6	8.5	13.1
2	2	6	70.7	61.0
3	2	6	6.6	7.4
4	2	6	57.2	50.8
6	2	6	60.6	61.9
7	2	6	10.4	10.6
8	2	6	47.5	47.5
10	2	6	38.2	39.5
2	-2	6	48.9	60.2
3	-2	6	10.7	10.7
4	-2	6	38.7	41.3
5	-2	6	8.4	4.3
6	-2	6	41.6	52.2
8	-2	6	31.0	37.8
10	-2	6	28.6	33.4
1	3	6	15.7	11.0
2	3	6	36.7	37.4
3	3	6	7.1	11.6
4	3	6	31.9	37.6
5	3	6	33.7	34.2
6	3	6	8.8	5.2
7	3	6	25.9	28.8
8	3	6	9.6	10.9
9	3	6	27.2	32.8
1	-3	6	29.5	34.6
2	-3	6	9.5	10.0
3	-3	6	28.6	42.9
4	-3	6	8.0	11.0
5	-3	6	29.4	39.0
6	-3	6	12.0	13.6
7	-3	6	27.8	35.9
8	-3	6	9.5	13.5
9	-3	6	28.2	34.3
12	-3	6	11.4	12.5
0	4	6	43.4	42.8
1	4	6	12.2	13.3
2	4	6	44.2	47.3
3	4	6	11.2	14.2
4	4	6	42.3	38.6
5	4	6	9.4	14.0
6	4	6	54.3	53.6
7	4	6	38.4	37.0
10	4	6	38.2	38.1
2	-4	6	33.6	42.7
3	-4	6	23.5	30.3
4	-4	6	9.3	3.4
5	-4	6	29.5	35.2
6	-4	6	20.3	26.3
7	-4	6	19.2	23.8
8	-4	6	15.1	11.1
1	5	6	29.6	33.1
2	5	6	14.0	9.7
3	5	6	23.9	29.9
4	5	6	12.5	4.4
5	5	6	27.6	27.1
6	5	6	10.6	3.3
1	-5	6	24.0	29.4
2	-5	6	8.8	10.1
3	-5	6	26.6	36.3
4	-5	6	12.0	9.5
5	-5	6	27.3	31.4
6	-5	6	27.5	30.9
0	6	6	20.1	24.3
1	6	6	9.8	9.6
2	6	6	21.7	32.8
3	6	6	10.5	13.1
4	6	6	19.5	22.8
12	0	6	29.7	34.5
13	0	6	30.6	30.9
16	0	6	19.6	20.5
12	1	6	12.7	16.7
13	1	6	23.3	24.7
15	1	6	22.3	24.8
16	1	6	15.8	12.6
12	-1	6	15.0	18.1
13	-1	6	24.0	26.2
14	-1	6	13.8	11.1
15	-1	6	21.5	26.6
12	2	6	33.1	37.4
14	2	6	20.0	33.4
12	-2	6	21.0	24.9
13	-2	6	22.3	26.4
14	-2	6	20.0	16.2
11	3	6	20.3	27.8
12	3	6	12.0	9.9
13	3	6	21.3	22.1
15	3	6	16.7	18.5
13	-3	6	21.5	26.4
14	-3	6	12.3	8.7
15	-3	6	27.9	22.6
12	4	6	30.2	31.6
12	-4	6	19.6	17.7
14	-4	6	16.7	18.7
7	5	6	21.4	22.2
8	5	6	11.2	6.6
9	5	6	18.7	23.9
11	5	6	20.3	21.1
12	5	6	12.7	6.6
13	5	6	12.4	14.6
8	-5	6	11.7	9.5
9	-5	6	18.9	26.8
10	-5	6	11.8	7.9
11	-5	6	21.2	26.7
12	6	6	11.5	15.2
6	6	6	28.1	38.3
7	6	6	11.9	15.0
8	6	6	16.8	25.2
9	-6	6	10.9	10.6
10	-6	6	18.7	27.5
11	-6	6	8.6	8.1
12	7	6	13.3	16.2
13	7	6	9.5	1.7
14	7	6	16.3	23.6
8	-6	6	9.3	13.5
9	-6	6	11.7	4.9
10	-6	6	12.6	16.7
11	7	6	13.2	5.4
12	7	6	16.2	24.2
13	7	6	14.3	9.2
14	7	6	17.3	23.5
15	7	6	16.7	21.4
12	-7	6	12.7	4.5
13	-7	6	18.2	16.7
14	-7	6	16.2	24.8
11	-7	6	11.5	11.9
12	8	6	13.8	24.6
13	8	6	13.6	25.3
14	-8	6	13.7	8.5
11	8	6	13.1	12.3
12	-8	6	13.1	8.1
13	-8	6	12.4	13.7
14	8	6	13.1	8.1
15	8	6	13.0	4.3
16	8	6	33.8	37.7
17	8	6	8.4	6.5
15	-8	6	39.4	40.4
16	-8	6	7.3	5.2
17	-8	6	38.9	28.1
18	-8	6	14.0	2.1
19	-8	6	37.7	36.0
16	9	6	9.8	0.6
17	9	6	28.0	20.0
18	9	6	14.9	9.4
17	-9	6	27.9	33.2
18	-9	6	23.3	22.6
19	-9	6	12.8	10.7
20	-9	6	9.8	17.3
2	-1	7	26.0	23.7
3	-1	7	5.6	5.4
4	-1	7	33.6	24.0
5	-1	7	14.2	11.9
6	-1	7	29.4	32.0
7	-1	7	12.6	2.1
8	-1	7	25.8	24.8
9	-1	7	11.3	14.4
10	-1	7	25.7	20.2
11	-1	7	12.2	6.8
1	2	7	58.2	39.5
2	2	7	48.6	36.8
4	2	7	14.6	6.5
5	2	7	44.8	35.9
6	2	7	30.6	30.3
7	2	7	10.9	2.5
8	2	7	25.8	30.0
9	2	7	39.8	32.9
1	-2	7	9.4	7.5
2	-2	7	37.1	34.2
3	-2	7	42.4	34.8
4	-2	7	28.3	24.6
7	-2	7	9.1	3.0
8	-2	7	25.6	21.1
9	-2	7	10.1	6.9
0	3	7	39.5	31.2
1	3	7	38.8	23.1
2	3	7	23.0	18.0
3

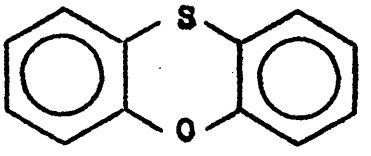
CHAPTER 4

DICHLOROBISPHENOXATHIINMERCURY(II)

4. DICHLOROBISPHENOXATHIINMERCURY (II)

4.1 Solution of the Structure.

When $HgCl_2$ and phenoxathiin:-



are dissolved in acetone/alcohol solution, yellow elongated plates of a complex crystallise out. When $HgBr_2$ is substituted for $HgCl_2$, the crystals which result are reddish-brown. On standing free to the atmosphere, the crystals break down in a day or two as the phenoxathiin evaporates and the mercuric halide is left behind. Provided a sufficient vapour pressure of the organic constituent is present, the crystals remain intact indefinitely.

From oscillation, pression and Weissenberg photographs the dimensions of the monoclinic cell of the complex were found to be: a = 31.00; b = 19.46; c = 3.95 Å; $\gamma = 111°18'$, the elongated axis of the crystal corresponding to the c-axis of the unit cell. The density of the crystal calculated on the assumption that the unit cell contains four units of $HgCl_2 \cdot (C_{12}H_8SO)_2$ is 1.57 gm.cc.$^{-1}$ That the density is near to this was confirmed by floatation in a solution of K_2HgI_4 in glycerol. (Owing to the high viscosity of the

solution, it was difficult to make an accurate measurement). The reflection conditions are: (hk0) present when h = 2n, k = 2n and (hkl) present when h+l = 2n. The space group is therefore Bb or B2/b. In addition to the systematic absences, the reflections are weak when k is odd. In the space group B2/b, occupation of the special positions 4a and 4b, $\bar{1}$, 0, 0, 1/2; 0, 1/2, 1/2; and 0, 0, 0; 0, 1/2, 0; restrict the contribution of that atom to general reflections for which k is even. Therefore the mercury atom must occupy such a position. The reflections to which it does not contribute fall off in intensity more quickly with increasing sin θ, than do the remainder.

Intensity data were collected for the layers hk0, hkl, and hk2, by means of equi-inclination Weissenberg photographs, using the multiple film, visual comparison technique already mentioned. Because of the short axis and certainty of complete resolution, the Patterson projection, P(uv), was computed (figure 10). All the important vectors involve Hg, Hg-C being of greater weight even than, for example S-S interactions. Since the Hg is situated at the origin, the Patterson has the appearance of a Fourier map and the entire structure is dramatically evident. In fact, since the ratio $A_{Hg}/\sum_n A_n$ where A_n is the atomic number, and the

summation is over all atoms other than Hg, is 6.1, it could have been safely assumed that the phases of all the structure factors (SFs) to which the Hg makes a contribution, would have been positive (e.g. Robertson, Phthalocyanine). A Fourier projection could then have been calculated straight away since the very reflections which have no Hg contributions are identically zero from space group symmetry.

All the atomic locations with arbitrary, but reasonably chosen temperature factors were used to calculate SFs. Satisfactory agreement with the F_o s was obtained, R = 0.190, and a Fourier F_o synthesis projection was then calculated from which improved co-ordinates for the light atoms were obtained. The use of these co-ordinates in recalculation of the hk0 intensities, resulted in no significant improvement in agreement, reflecting the relative unimportance of the light atom co-ordinates on the magnitude of F_c compared to the Hg whose co-ordinates were known with complete accuracy. Other than this one F_o map, no attempt was made to refine the projection. A difference map was, however, calculated, and this showed that the Hg atoms was vibrating anisotropically. A two electron peak showed up at the sulphur location, but the remainder of the map was free of significant undulations.

In three dimensions, the Patterson space group is P2/m, so there exists a choice of locations for all atoms other than mercury and any one other. From the 3-D Patterson, the Cl atom was fixed at (0.02908, -0.06852, -0.34177) and the O atom was fortuitously near z = 0. The S atom was allocated z co-ordinates of $\pm$0.20267 in two different S.F. calculations on a few Fs for which l $\neq$ 0. The co-ordinate producing the better agreement was taken as giving the position of the S correctly relative to the Hg, Cl and O. The z co-ordinates of all the C atoms differed from zero and while it might well have been possible to disentangle the molecule from its mirror image it was decided that it would be quicker and surer to circumvent the problem. Consequently S.Fs based on the Hg, Cl, S and O positions were calculated and gave an agreement index of 0.284. A few of these F_cs which agreed poorly with the F_os were rejected, and the remainder used to calculate a three dimensional Fourier synthesis. This showed all the atoms clearly, with no trace of peaks related by a mirror at z = 0. Inclusion of these co-ordinates into a further round of S.F. calculations resulted in a drop in R of 0.055 to 0.229. One final F_o map was calculated with all terms included, and co-ordinates derived from this used as a starting point in the least-squares refinement of

the structure,

Refinement. Refinement of this structure was carried out on a IBM-7090 computer, using the structure factor least square programme, ORFLS, written by W.R. Busing and H. A. Levy. The details of the programme are well known. (Busing, Martin and Levy, 1962).

It has the advantage over other least squares programmes used in this work, that it was able to refine a number of scale factors.

The data were repunched in a form suitable for the IBM-7090. Initial co-ordinates were taken from the second, three-dimensional F_o synthesis, and the temperature factors were given the original, arbitrary values: (U_{iso}):

Hg = 0.023, S and Cl = 0.034, O and C = 0.043 $\mathring{A}^2$

The scale factors were obtained from the last cycle of structure factor calculation, by making

$\sum k |F_o| = \sum |F_c|$ for each layer of 1.

The weighting scheme used was again Rollett's:

$\sqrt{w} = 1$ for $|F_o| < 15$, and $\sqrt{w} = 15/|F_o|$ for $|F_o| > 15$.

Three cycles of full matrix, isotropic refinement, were sufficient to produce convergence. The R value dropped to 0.172 on the first cycle, to 0.159 on the second, and 0.158 on the third. That the weighting scheme

was inadequate, was shown by a final value of

$$R_1 = \sum w\Delta^2 \Big/ \sum w[|F_o| k]^2$$

of 0.207.

The three scale factors were highly correlated as shown by coefficients of approximately 0.50. The correlation coefficients between the scale factors and the temperature factor of the mercury, are in the region of 0.7.

The weighting scheme was changed to:

$$w = 1/(P_1 + F_o + P_2 F_o^2 + P_3 F_o^3)^{1/2}$$

with the values $P_1 = 25$, $P_2 = 3.636 \times 10^{-3}$, $P_3 = 1.653 \times 10^{-5}$. Two cycles of anisotropic refinement with this weighting scheme brought R to 0.1115 and R' to 0.0226.

4.2 Description of the Structure.

The mercury is situated on a centre of symmetry. It is six-co-ordinate , and has two chlorine atoms at 2.33Å, two at 3.08Å, and the two sulphur atoms of the ligand at 3.12Å. The angles at the mercury, are close to 90°. The mercury atoms of adjoining, distorted octahedra, are 3.95 Å apart, (the c-axis repeat distance), and are linked by unsymmetrical, non-linear, chlorine bridges. A closely bonded chlorine belonging to one octahedron, is identical with a loosely bonded chlorine of the next.

The structure is therefore a linear array of distorted octahedra sharing opposite edges. In this arrangement of ligands, the structure is similar in type to others found previously, and illustrates one of the well known ways in which such polyhedra pack, (Damm and Weiss, 1955).

The almost planar ligands lie nearly normal to the c-axis, and therefore the six-membered rings lie neatly in between the Hg-Cl bonds. The ligand dimensions are no different from these expected in the uncomplexed phenoxathiin. The dihedral angle between the two benzene rings is 153.1° which compares with the value of 155 ± 5° deduced from the dipole moment of phenoxathiin by Leonard and Sutton (1948). The angles subtended at the sulphur are approximately tetrahedral. There appears

to be no interaction between phenoxathiin ligands on different mercury atoms.

Figure (11) shows the structure projected down [001]. Figure (12) illustrates the immediate environment of a mercury atom.

Figure 10.

DICHLOROBISPHENOXATHIINMERCURY (II). The two-dimensional Patterson function, P(u,v). The contour levels are arbitrary.

Figure 10.

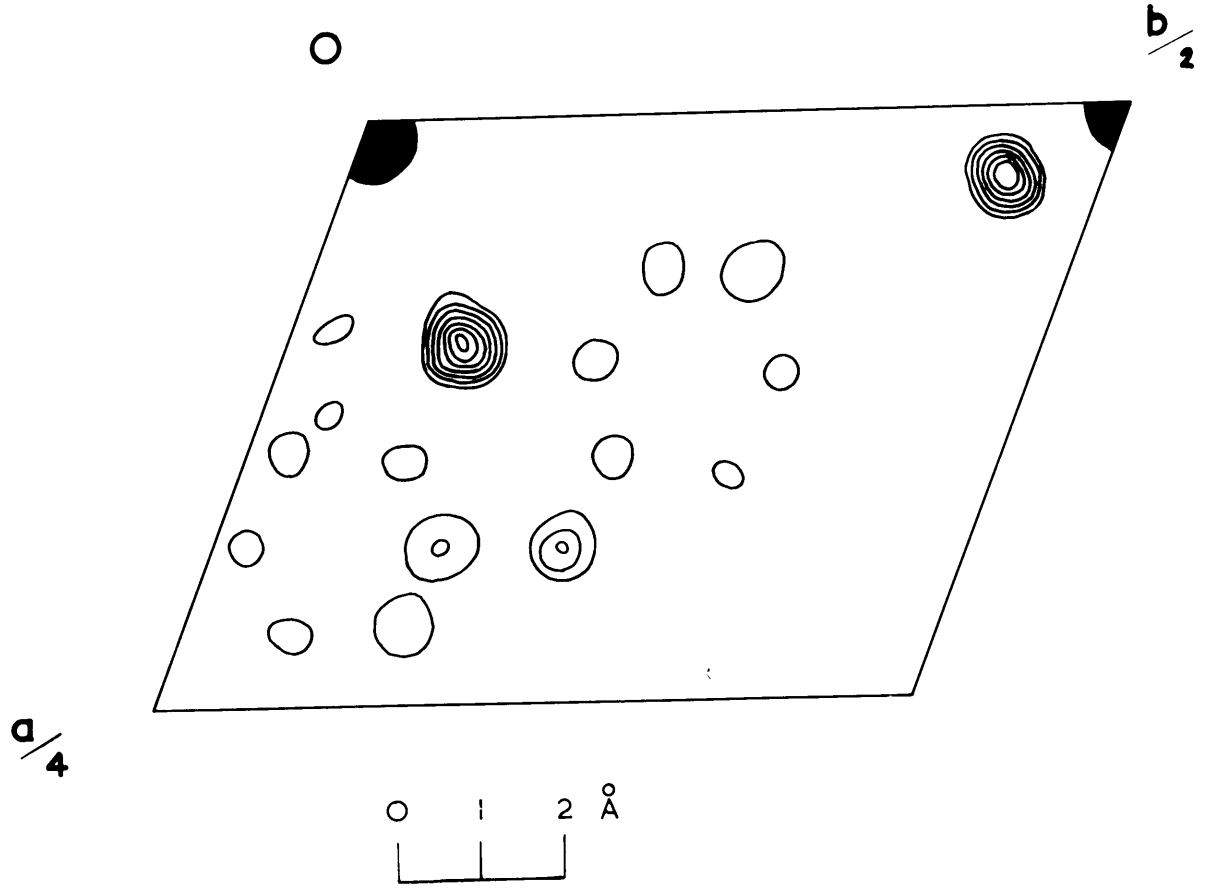


Figure 11.

DICHLOROBISPHENOXATHIINMERCURY (II). Projection of the structure down the c-axis.

Figure 11.

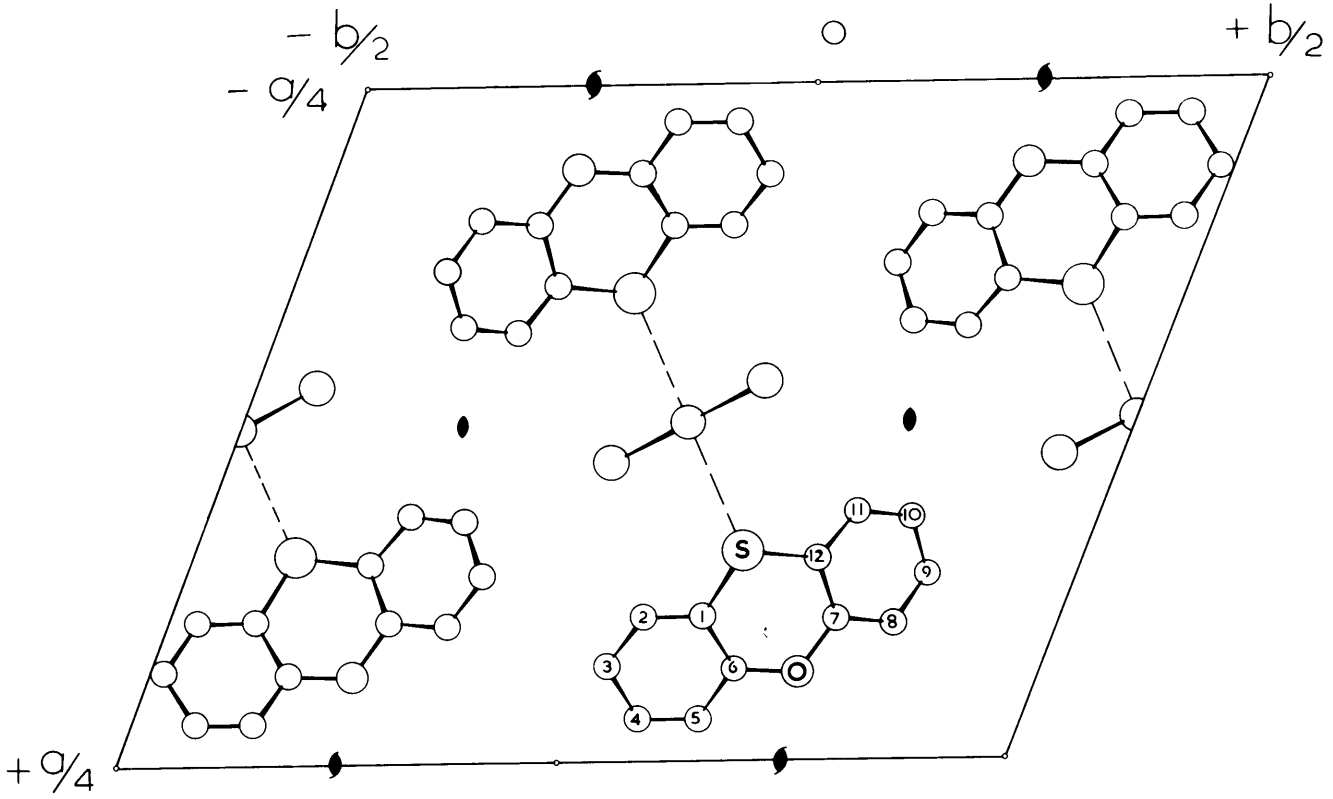
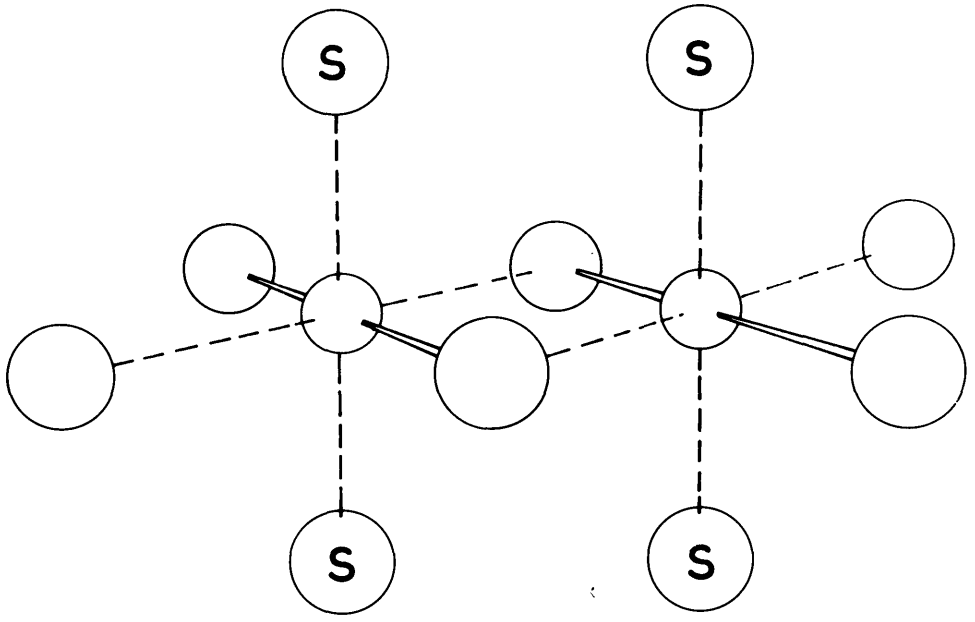


Figure 12.



The immediate environment

of the mercury atom

Figure 13.

Visible absorption spectra of DICHLORO- and DIBROMO-BISPHENOXATHIINMERCURY (II) in the solid state.

Figure 13.

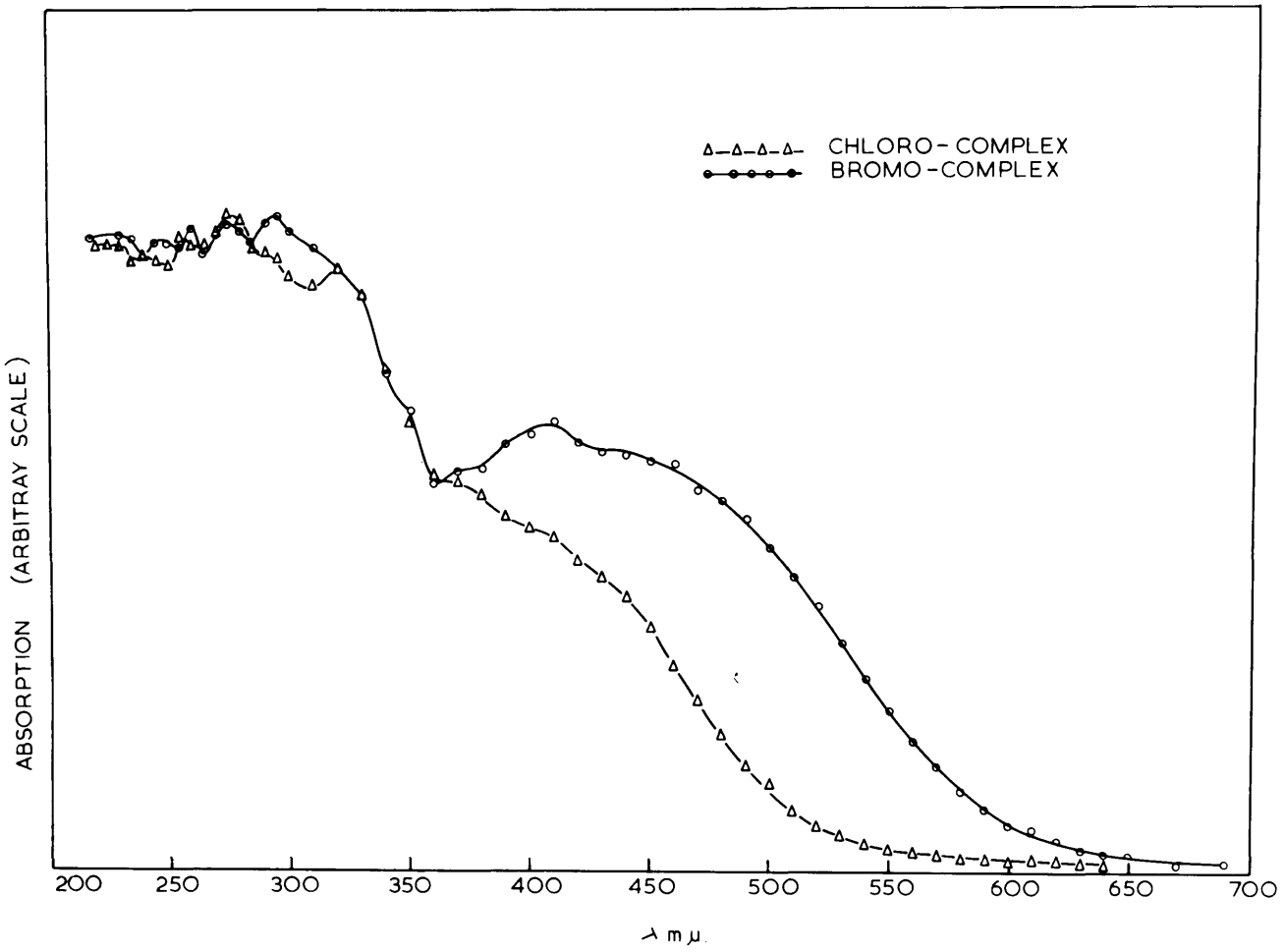

Δ–Δ–Δ–Δ– CHLORO-COMPLEX
BROMO-COMPLEX
ABSORPTION (ARBITRAY SCALE)
200
250
300
350
400
450
500
550
600
650
700
λ mμ

TABLE (13)

DICHLOROBISPHENOXATHIINMERCURY (II)

Fractional Atomic Co-ordinates

Atom	x	y	z
Hg	0.00000	0.00000	0.00000
Cl	0.02956	-0.06496	-0.36922
S	0.09599	0.12003	0.17286
O	0.18475	0.22978	-0.13061
C(1)	0.14281	0.10190	-0.00852
C(2)	0.14311	0.03263	-0.01422
C(3)	0.18112	0.01483	-0.14061
C(4)	0.21742	0.07008	-0.27489
C(5)	0.21910	0.14257	-0.26774
C(6)	0.18137	0.15728	-0.13990
C(7)	0.14602	0.24825	-0.16522
C(8)	0.15010	0.31429	-0.31280
C(9)	0.11249	0.33702	-0.34359
C(10)	0.06890	0.29344	-0.22968
C(11)	0.06523	0.22481	-0.09203
C(12)	0.10242	0.20316	-0.04786

TABLE (14)

DICHLOROBISPHENOXATHIINMERCURY (II)

Estimated Standard Deviations of Fractional Atomic Co-ordinates

Atom	(x)	(y)	(z)
Hg	0.00000	0.00000	0.00000
Cl	0.00022	0.00036	0.00268
S	0.00020	0.00034	0.00270
O	0.00063	0.00100	0.00835
C(1)	0.00082	0.00146	0.00966
C(2)	0.00117	0.00198	0.01150
C(3)	0.00106	0.00193	0.01382
C(4)	0.00102	0.00192	0.01469
C(5)	0.00084	0.00178	0.01184
C(6)	0.00074	0.00141	0.01096
C(7)	0.00092	0.00143	0.01113
C(8)	0.00108	0.00149	0.01404
C(9)	0.00120	0.00162	0.01279
C(10)	0.00111	0.00152	0.01288
C(11)	0.00116	0.00177	0.01277
C(12)	0.00094	0.00146	0.00969

TABLE (15)

DICHLOROBISPHENOXATHIINMERCURY (II)

Anisotropic Thermal Parameters ($Å^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
Hg	0.05791	0.05200	0.05860	-0.00540	0.00192	0.03295
Cl	0.04395	0.04370	0.01370	-0.00087	0.00342	0.01987
S	0.02759	0.03327	0.03030	-0.00136	0.00045	0.00704
O	0.03576	0.03251	0.08235	0.00495	0.00493	-0.00697
C(1)	0.02615	0.03454	0.07086	-0.00532	-0.00117	0.00329
C(2)	0.04771	0.05054	0.07987	0.00615	-0.00550	0.00171
C(3)	0.04416	0.06099	0.06610	-0.00502	-0.01006	0.01562
C(4)	0.04256	0.06704	0.08456	0.00063	-0.00309	0.02133
C(5)	0.02691	0.06762	0.04366	-0.00236	-0.00101	0.00341
C(6)	0.01698	0.03787	0.06085	0.00842	-0.00103	-0.00527
C(7)	0.04095	0.03780	0.02251	0.00136	0.00096	0.00116
C(8)	0.05699	0.03132	0.08099	0.00671	0.00769	0.00642
C(9)	0.07306	0.04281	0.04132	0.00994	0.00853	0.02857
C(10)	0.06728	0.04094	0.06012	-0.00051	0.00515	0.02177
C(11)	0.05679	0.04685	0.06210	0.00717	0.00039	0.01751
C(12)	0.04061	0.03545	0.03508	-0.00305	-0.00358	0.00430

TABLE (16)

DICHLOROBISPHENOXATHIINMERCURY (II)

Interatomic Bond Lengths in Å with Estimated Standard Deviations

Bond		Length	E.s.d.
Hg	- Cl	2.325	(0.008)
Hg	- Cl'	3.080	(0.003)
Hg	- S	3.119	(0.006)
S	- C(1)	1.765	(0.029)
S	- C(12)	1.784	(0.032)
O	- C(6)	1.377	(0.035)
O	- C(7)	1.380	(0.033)
C(1)	- C(2)	1.352	(0.049)
C(2)	- C(3)	1.433	(0.052)
C(3)	- C(4)	1.351	(0.052)
C(4)	- C(5)	1.393	(0.048)
C(5)	- C(6)	1.396	(0.041)
C(6)	- C(1)	1.387	(0.038)
C(7)	- C(8)	1.375	(0.047)
C(8)	- C(9)	1.394	(0.045)
C(9)	- C(10)	1.384	(0.050)
C(10)	- C(11)	1.408	(0.048)
C(11)	- C(12)	1.375	(0.044)
C(12)	- C(7)	1.396	(0.041)

TABLE (17)

DICHLOROBISPHENOXATHIINMERCURY (II)

Interbond Angles with Estimated Standard Deviations

Atoms			Angle	E.s.d.
Cl	- Hg	- Cl'	87.16°	(0.27°)
Cl	- Hg	- S	79.20°	(0.22°)
Cl'	- Hg	- S	81.99°	(0.21°)
C(1)	- S	- Hg	113.0°	(1.0°)
C(12)	- S	- Hg	109.5°	(1.0°)
C(1)	- S	- C(12)	98.8°	(1.5°)
C(6)	- O	- C(7)	121.0°	(2.0°)
C(6)	- C(1)	- S	122.4°	(2.2°)
C(2)	- C(1)	- S	120.7°	(2.4°)
C(2)	- C(1)	- C(6)	116.9°	(2.7°)
C(1)	- C(2)	- C(3)	123.4°	(3.2°)
C(2)	- C(3)	- C(4)	117.7°	(3.3°)
C(3)	- C(4)	- C(5)	120.8°	(3.4°)
C(4)	- C(5)	- C(6)	119.3°	(2.8°)
C(5)	- C(6)	- C(1)	121.7°	(2.7°)
C(1)	- C(6)	- O	120.6°	(2.5°)
C(5)	- C(6)	- O	117.5°	(2.4°)
O	- C(7)	- C(8)	119.5°	(2.6°)
O	- C(7)	- C(12)	122.6°	(2.8°)
C(8)	- C(7)	- C(12)	117.9°	(2.6°)
C(7)	- C(8)	- C(9)	122.0°	(3.1°)

TABLE (17) (Contd)

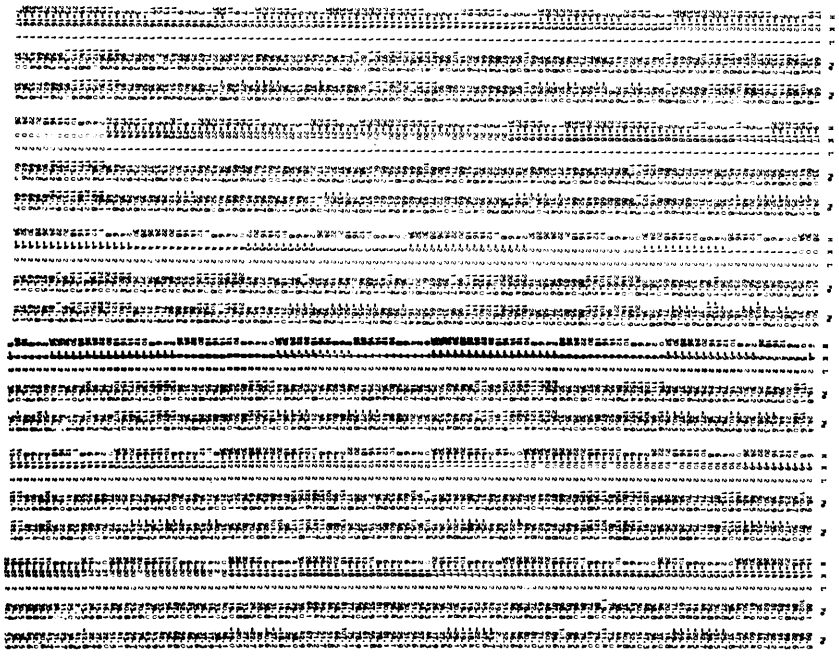
Atoms	Angle	E.s.d.
C(8) - C(9) - C(10)	121.3°	(3.1°)
C(9) - C(10) - C(11)	115.6°	(2.8°)
C(10) - C(11) - C(12)	123.5°	(3.1°)
C(11) - C(12) - C(7)	119.6°	(3.0°)
C(11) - C(12) - S	120.7°	(2.5°)
S - C(12) - C(7)	119.7°	(2.2°)

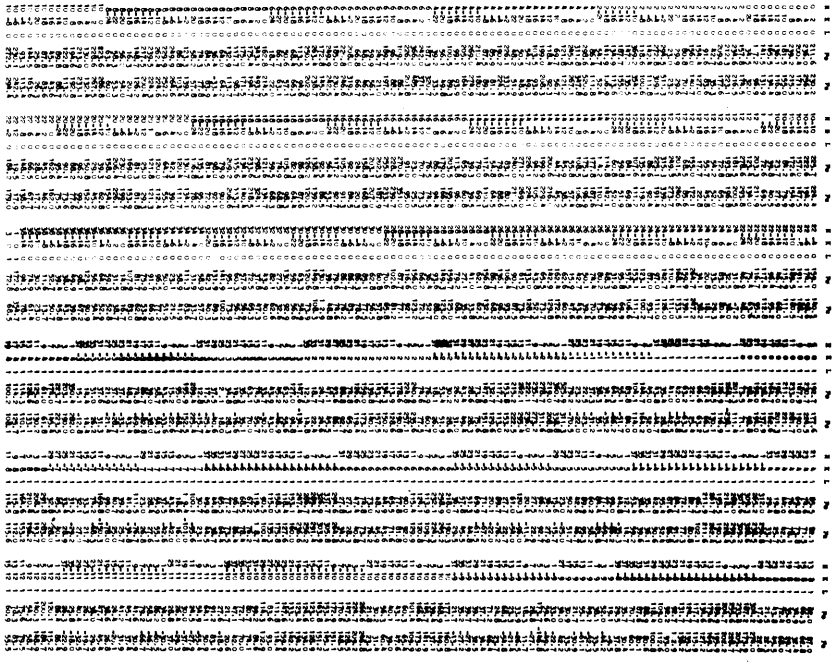
TABLE (18)

DICHLOROBISPHENOXATHIINMERCURY (II)

Observed and calculated

structure factors.





4.3 Discussion of the Structure.

Mercuric halide structures in which compounds containing a ring sulphur or a ring oxygen atom are co-ordinated to the metal are known (Hassel and Hvoslef, 1954; Cheung and Sim, 1964).

Phenoxathiin contains a ring sulphur and a ring oxygen atom in similar environments, and therefore both of them are potentially available for complexing to a metal atom. It is of interest to see which atom in such a system is actually used, or whether the ligand is bidentate. It is to be expected that the complexing power of both sulphur and oxygen atoms would, to some extent, be modified by the presence of the other. Because the two atoms might be said to be competing against one another, the ligand was expected to be loosely bonded to the mercury.

The solution of the crystal structure has revealed that there are indeed no strong bonds formed between the metal and phenoxathiin molecule, and that the sulphur atom is preferred to the oxygen for co-ordinating. The distance between the mercury and sulphur atoms, indicates very weak bonding, which is evidenced by the ready decomposition of the crystals on standing in air, or on solution in any solvent. The Hg-S length is slightly less than the sum of van der Waal's radii.

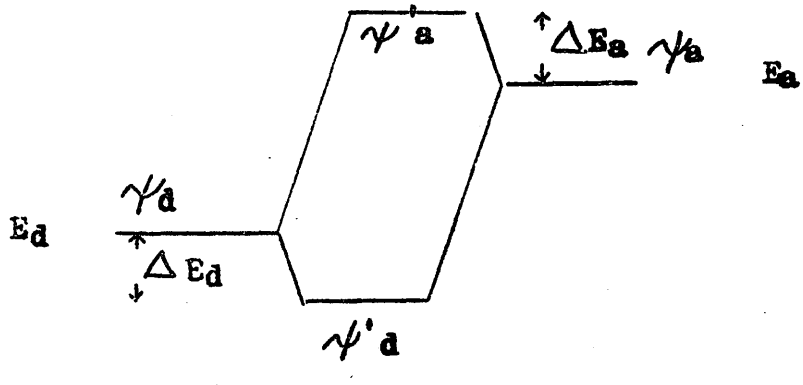
Although the interaction is so tenuous, it does have the effect of giving the crystalline complex an absorption band in the visible region, which is exhibited by neither of the components. The development of completely new, intense absorption bands, when seemingly non-reacting compounds are mixed, is well known, the most famous example being, perhaps, the benzene-iodine system (Benesi and Hildebrand, 1949).

It has been shown (Mulliken, 1950, 1952a, 1952b), that this absorption can be accounted for by assuming a degree of charge transfer from one component, D, of such a system, to the other, A. The wave functions for the complex can be expressed as a combination of the function ψ_d, for the ground state D, A, and the function ψ_a, for the charge transfer state, D^+, A^-. One state of the complex is mainly ψd, the other mainly ψ_a.

$$\psi'_d = \psi_d + \lambda_{ad}\psi_a$$

and

$$\psi'_a = \psi_a + \lambda_{da}\psi_d$$



Transitions between ψ_d' and ψ_a', are responsible for the absorption. The stabilisation of the ground state is:

$$-\Delta E_d = \lambda_{ad}^2 (E_a - E_d),$$

and the elevation of the charge transfer state is:

$$\Delta E_a = \lambda_{da}^2 (E_a - E_d).$$

Therefore, approximately, the energy of the transition depends on the difference, $(E_a - E_d)$. If E_a is large and E_d small, this means that the ionisation potential of the donor must be high and the electron affinity of the acceptor slight. That is, not allowing for environmental factors, the frequency of absorption is directly dependent on the difference $(I_D - E_A)$. The subject is reviewed by Murrell (1961) and Orgel (1954).

This relationship has been observed in a large number of organic charge transfer systems, for example, those tabulated by Brackman (1949). It is also observed in many metallic halides, where the transfer occurs from halide to metal ion. In particular, it holds for the chloride, bromide and iodide of mercury, the absorption frequency decreasing in that order as, I_D, the ionisation potential of the halogen donor, decreases.

The solid state spectra of the bromo and chloro complexes are shown in figure (13). Absorption bands extend from below 200 mμ into the visible, the bromo

band continuing to a greater wavelength than the chloro band. If the phenoxathiin complexes are charge transfer complexes, with the sulphur ligand acting as the donor, and the mercury halide as the acceptor, we might expect E_A to be lower for the bromo, than for the chloro-compound, and consequently the frequency or energy of transition to be greater. This, however, is not the case, the bromo-compound showing absorption at lower frequency than the chloro. In other words, the situation remains as in the mercuric halides themselves as expected for halide to metal transfer, but the bands have been shifted to the visible.

This appears to imply that complexing with the phenoxathiin has facilitated the halide to metal transfer, and that the sulphur ligand acts to some extent as an acceptor.

Although the extinction coefficient in solution could not be measured, and apparatus of single crystal spectroscopy was not available, the intensity of absorption did not seem to be very high. This toosuggests that the absorption is not due to a simple sulphur-ligand to metal charge transfer.

It is possible to obtain absorption when there is no net transfer of charge. For example, a system of identical components, A, A, may be stabilised by equal

contribution from the states $A^{+}A^{-}$ and $A^{-}A^{+}$. The $Ag^{+}C_6H_6$ system is believed to receive a contribution from $Ag^{2+}C_6H_6^{-}$ (Murrell, 1961). By analogy with this case, it might be that in the phenoxathiin adduct, metal to sulphur π^{*} orbitals charge transfer does occur in addition to sulphur σ metal transfer.

CHAPTER 5

DISCUSSION OF THE STRUCTURES

5. DISCUSSION OF THE STRUCTURES.

Thiourea is known to co-ordinate readily with a large number of metals, and several complexes have been examined crystallographically. (Truter, 1958 (a), 1963, Nardelli and Fava, 1959, Nardelli, 1957, Braibanti and Fava, 1959). Short sulphur to metal bonds are always found. It is therefore not surprising to find covalent mercury to sulphur distances in the complexes described above. The co-ordination of the mercury is unusual. An obvious postulate for the structures of these compounds would have been one having a very distorted tetrahedal arrangement around the mercury, similar to that found in, for example, $HgCl_2$ $2[(C_6H_5)_3 AsO]$ (Brändén, 1963). It is curious to note that an essentially three-co-ordinate structure could have reasonably been expected for the mercuric chloride adduct of 1, 6- dithiacyclodeca-cis-3, cis-8-diene, $2(HgCl_2)$ $S_2C_8H_{12}$, (Cheung, 1964), whereas the actual structure comprises one distorted tetrahedral mercury, and one almost unperturbed mercuric chloride molecule. These examples emphasise the extremely unpredictable nature of mercury complex structure.

The only generalisation which can be made about the co-ordination the mercury will adopt in any given structure is that, if the ligand is highly basic, three or four ligands will be closely bonded to the mercury.

Weakly basic ligands result in structures in which the mercury is octahedrally surrounded, and has two short linear bonds, and four bonds of length rather less than the sum of the van der Waal's radii. This difference of type is illustrated in table (A).

However, given the structure of a complex, it is possible to rationalise the dimensions on the basis of the relative electronegativities of the various ligands. Bent (1961) has pointed out that, for light atoms using sp^3 hybrid orbitals, the bonds do not necessarily all contain the same amounts of S character, but this concentrates in those bonds directed towards the least electronegative ligands. He uses these so-called second order hybridisation effects to account for the variation in bond lengths and angles in series of compounds, such as halogenated methanes.

Fractional s character of atomic orbitals used in bonding to ligands, may be calculated from a knowledge of the angle between the bonds. Let two bonds be described by the following s-p hybrids of the central atom:

$$\begin{aligned} &(1 - S_1^2)^{1/2} \psi p_1 + S_1 \psi_s \\ &(1 - S_2^2)^{1/2} \psi p_2 + S_2 \psi_s \end{aligned} \qquad (A)$$

The wave functions ψ_{p_1} and ψ_{p_2} refer to p states of the atom, symmetric about the two bond directions, and ψ_s refers to the s state. Since the two bonds must be independent of each other, the two states must be orthogonal. If θ is the angle between the bonds then,

$$\int \psi_{p_1} \cdot \psi_{p_2} \, d\tau = \cos\theta,$$

$$[(1-S_1^2)^{1/2} (1-S_2^2)^{1/2} \cos\theta] + \int [(1-S_1^2)^{1/2} S_2 \psi_s \psi_{p_1} + S_1 S_2 \psi_s^2 + (1-S_2^2)^{1/2} S_1 \psi_s \psi_{p_2}] = 0$$

If the two bonds are equivalent, so that

$$S_1 = S_2 = S$$

then, $$[(1-S^2) \cos\theta + S^2] = 0$$

and $$S^2 = \frac{\cos\theta}{\cos\theta - 1}$$

gives the fraction of s character in each bond.

In the case of mercury complexes, we are no longer dealing with a simple atom, and the atomic hybrid orbitals used in bonding are not necessarily mixtures of s and p functions only. Although d-orbitals may be used in σ-bonding, the result given above remains thesame, and we shall not consider d-orbitals explicitly.

In dichlorobisthioureamercury (II), the angle between the equivalent mercury-sulphur bonds is 139° 00′

and the fractional s character in each bond is therefore 0.43. Assuming that the mercury uses its s orbital and two p orbitals in bonding to the two sulphur ligands and the one chlorine atom lying in the same plane, and that the interaction with the remaining chlorine atoms is largely ionic, it is possible to say that the mercury-chlorine covalent bond must possess 0.14 s character. The bond is 2.58 Å in length. With these figures, it is now instructive to compare the mercury-chlorine bond length with lengths found in other structures.

Mercuric chloride itself, approximates to a molecular crystal containing discrete linear $HgCl_2$ units, with a mercury-chlorine separation of 2.25 Å. A determination in the gas phase, has given 2.29 Å as the bond length in mercuric chloride, (Akishin et.al., 1959). Here the fractional s character in each bond is 0.50.

Discrete $HgCl_4^{2-}$ ions, which are nearly tetrahedral, are found in the crystal of the mercuri—chloride of perloline, (Jeffreys et.al., 1963). Averaging bond angles and lengths, gives a separation of 2.50 Å corresponding to bonds containing 0.25 s character. This distance is also found in the mercuric chloride adduct of 1, 6- dithiacyclodeca-cis-3, cis-8-diene, (Cheung

et.al., 1964), where the fractional s character in the mercury-chlorine bond is calculated to be 0.25.

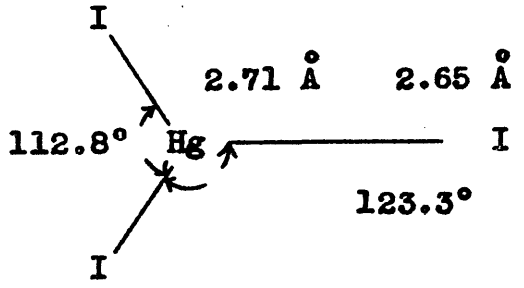
The structure of dichlorobisthioureamercury (II) therefore, helps to show that Bent's observation provides a useful rationalisation of heavy atom structures also, since the chlorine atom is clearly more electronegative than the sulphur in the thiourea group. It is also clear that the exceptionally long mercury-chlorine bond is in keeping with the steady increase in length as the amount of s character in the bond decreases from compound to compound.

Table (A) summarises some data relevent to mercury-chlorine bond length variation.

The data for other mercury bonds are not so extensive. The mercury-bromine distance corresponding to bonds of 0.50 s character, has been determined as 2.41 Å in the gas phase, (Akishin et. al., 1963). This agrees with the value (2.44 Å) obtained in the linear Br-Hg-SCN molecule, (Zvonkova and Zhdonov, 1952). The structure of $(CH_3)4\ N\ HgBr_3$ contains recognisable planar $[HgBr_3]^-$ ions, (White, 1963), which can be considered,for this approximate treatment, to be isolated. The average mercury-bromine bond length is 2.52 Å, which therefore represents a bond with s = 0.33. A value close to this (2.6 ± 0.1 Å) is found in $Hg_3\ NHBr_2$

(Brodersen, 1955), in which the mercury has trigonal bipyramidal co-ordination, the axial being much longer. Finally, dibromobisthioureamercury (II) exhibits a mercury-bromine distance of 2.81 Å, which can be taken as representing a bond with very little (s = 0.05) s character.

Mercury iodine bond lengths are known from the two modifications of mercuric iodide, and the compound $(CH_3)_3S\ Hg\ I_3$. The yellow form of mercuric iodide has linear I-Hg-I units, (s = 0.50), the bond length is 2.62 Å, (Gorskii, 1934). Mercury atoms are tetrahedrally co-ordinated in the red form, in which the bond length is 2.78 Å, (Huggens and Magill, 1927), corresponding to s = 0.25. $(CH_3)_3S\ Hg\ I_3$ contains $[HgI_3]^-$ ions, which are planar, (Fenn, Oldham and Phillips, 1963).



The long Hg - I distances correspond to s = 0.28, the short one to s = 0.44

Mercury-sulphur compounds constitute the only other group for which there is much data. The S-Hg-S

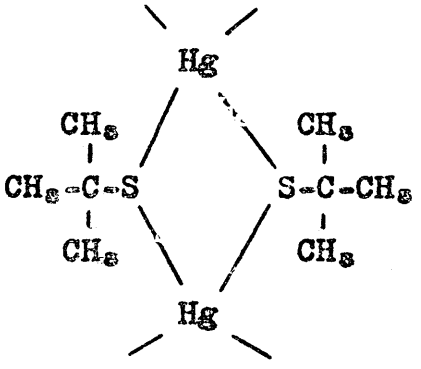
bond angles in the dibromo- and dichlorobisthiourea-mercury (II) are respectively 144.5° and 139.0°, (s = 0.45 and 0.43). The bond lengths are, however, 2.43 Å for the bromo-compound and 2.37 Å for the chloro-compound. The differences appear to be significant (σ = 0.01 - 0.02 Å). This discrepancy may be connected with the observation that the 'effective' co-ordination of the mercury in the bromo-compound is higher than that in the chloro-compound. The term 'effective' ligand has been used by Grdenić (1965) to describe one which lies at a distance from the mercury appreciably less than the sum of the van der Waal's radii of the mercury and ligand atom. The sum of the van der Waal's radii of mercury and chlorine is 3.30 Å. The Hg-Cl (2) distance found (3.22 Å) is only slightly less than this. The sum of the radii of mercury and bromine is 3.45 Å, and in the bromo-compound, the four Hg-Br distances are: 2.81 Å, 3.00 Å, 3.33 Å and 3.41 Å. Therefore the effective co-ordination in the chloro-compound is three or slightly more, while it is four to five in the bromo-compound.

The value given by Harding (1958), for the mercury-sulphur length in the mercury dithiazone complex is 2.4 ± 0.1 Å. The S-Hg-S angle of 155° implies s = 0.48.

As stated by Brändén, the mercury-sulphur bond

length varies from 2.36 Å to 2.52 Å as delimited by many examples of linear S-Hg-S bonds (s = 0.50) and tetrahedral angle S-Hg-S bonds (s = 0.25), table (A). It can be added that for bonds of an intermediate nature, the length is around 2.4 Å.

There is a particularly long bond between mercury and sulphur in the structure of $HgSC(CH_3)_3$, (Bradley and Kunchur, 1964). This is an infinitely extended spiro structure.



Hg-S = 2.59 ± 0.03 Å
2.66 ± 0.03 Å
S-Hg-S = 87 ± 1.5°
90 ± 1.5°
121 ± 1.5°

The bond angles suggest that the bonds are pure p or even bent to some extent.

Linear Hg-O bonds are found in HgO, (Aurivillius, 1956), $Hg_3 O Cl_4$, (Šćavničar and Grdenić, 1955). The bond length is 2.03 Å. In $Hg_3 O_2 Cl_2$, (Šćavničar, 1955), the Hg-O bonds have an average length of 2.16 Å, and the average of the O-Hg-O bond angles implies, s = 0.30. An example of a Hg-O bond containing very little s character is found in $Hg Cl_2 2(C_6H_5)_3 AsO$, (Brändén, 1963).

When mercury is surrounded by N and Cl atoms, the poorly co-ordinating N is relegated to a distant site of a distorted octahedron, while the chlorines are used for bridging in a manner similar to that in the phenoxathiin adduct, ($HgCl_2$ 2 NC_5H_5, Grdenić, Krstanović, 1955). In the mercury dithiazone complex too, the N atoms are only weakly bonded to the metal, but the angles in this molecule result from the dimensions of the thiazone grouping. Short linear N-Hg-N bonds are found in the compound $Hg(NH_3)_2Cl_2$, (MacGillavry and Bijvoet, 1936) where the chlorine is largely ionic. The N-Hg distance corresponding to $s = 0.50$ is 2.07 Å.

In the light of these investigations, it appears that the Hg-Cl bond length varies just as much as the Hg-S, when the mercury hybridisation is sufficiently altered. Indeed bond length changes are observed no matter what atom is bonded to mercury, and we believe that these changes can be directly linked with the relative donating powers of the various ligands on the complexed atom. This treatment involves averaging some bond lengths and angles and is not intended to give more than a qualitative explanation for the observed structures. Its justification lies in the systematisation it confers on a subject which is too complex to be

treated other than empirically.

The experimental data are too complex to permit speculation on the possibilities of π-bonding in these complexes. Cotton, however, has considered it worth while to point out which orbitals may be possibly used for this purpose (1960). We shall therefore do the same for the more symmetrical of the thiourea complexes studied.

Owing to the very great separation of the bridging chlorine atom in dichlorobisthioureamercury (II) it is justifiable to leave them out of consideration in covalent bonding. (The Hg-Cl distance is 3.22 Å. The ionic radii of mercury and chlorine are 1.40 Å and 1.81 Å respectively). The symmetry of the molecule, with or without these chlorines is C_{2v}. The (group theory) character table for this point group is:

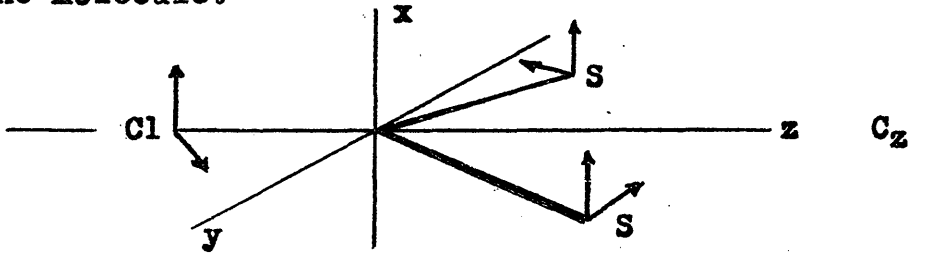
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

(The z axis is the two-fold axis).

A representation for the σ-bonds is readily found to be:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ_σ	3	1	1	3

This is reducible to, $\Gamma_\sigma = 2A_1 + B_2$.
The available ligand orbitals are filled σ orbitals of the sulphur and chlorine atoms, and unoccupied 3d orbitals. The metal orbitals are the 5d, 6s and 6p. The three ligand σ orbitals, therefore span A_1 and B_2. The ligand π bonding orbitals may be represented by vectors parallel to and perpendicular to the plane of the molecule.



A representation for the π-bonding orbitals, and the two sets into which it can be broken are:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz$
Γ_π	6	-2	0	0
$\Gamma_\pi \perp$	3	-1	1	-3
$\Gamma_\pi \parallel$	3	-1	-1	3

These are reducable as follows:

$$\Gamma_{\perp} = A_2 + 2B_1$$
$$\Gamma_{\parallel} = A_1 + 2B_2$$

The nine valency shell orbitals of the mercury atom correspond to the irreducible representations in the following manner:

A_1 s , p_z , d_z^2 .

A_2 d_{xy} .

B_1 p_x , d_{xz} .

B_2 p_y , d_{yz} .

Therefore σ-bonding orbitals may be compounded in any of the six ways involving two orbitals of the set S, p_z , dz^2, and one of the set p_y , d_{yz}. This leaves the orbitals dxy, and p_x , d_{xz} completely free to participate in π-bonding. Orbitals belonging to A_1 and B_2 would presumably be preferentially used in σ-bonding.

TABLE (A)

Compound	Hg-Cl (Å)	s	Ref
$HgCl_2$	2.29	0.50	3
$K_2HgCl_4.2H_2O$	2.29	0.50	89
Hg_3OCl_4	2.28	0.50	74
$CsHgCl_3$	2.29	0.50	89
CH_3HgCl	2.282	0.50	27
$[HgCl_2.(C_6H_5)_3AsO]_2$	2.32	0.46	14
$HgCl_2.2(C_6H_5)_3AsO$	2.32	0.45	13
$C_{20}H_{17}N_2O_3,1/2(HgCl_4)H_2O$	2.50	0.25	40
$2HgCl_2.S_2C_8H_{12}$	2.51	0.25	18
$HgCl_2[(NH_2)_2CS]_2$	2.58	0.14	-
$Hg_3O_2Cl_2$	2.66	0.10	73

Compound	Hg-Br (Å)	s	Ref
$HgBr_2$	2.41	0.50	3
HgBrSCN	2.44	0.50	90
$(CH_3)_4NHgBr_3$	2.52	0.33	83
Hg_2NHBr_2	2.6	0.33	12
$HgBr_2[(NH_2)_2CS]$	2.82	0.05	-

Compound	Hg-I (Å)	s	Ref
HgI_2 (yellow)	2.62	0.50	28
$(CH_3)_3SHgI_3$	2.65	0.44	25
$(CH_3)_3SHgI_3$	2.71	0.28	25
HgI_2 (red)	2.78	0.25	39

TABLE (A) (contd)

Compound	Hg-S (Å)	s	Ref
HgS (cinnabar)	2.36	0.50	4
$Hg(SCH_3)_2$	2.36	0.50	9
$HgCl_2[(NH_2)_2CS]_2$	2.37	0.43	-
$HgBr_2[(NH_2)_2CS]_2$	2.43	0.45	-
$Hg(C_{15}H_{11}N_4S)_22(C_5H_5N)$	2.41	0.48	32
HgS (metacinnabar)	2.52	0.25	4
$Cuen_2Hg(SCN)_4$	2.55	0.25	74
$2HgCl_2.S_2C_5H_{12}$	2.53	0.25	18
$CuHg(SCN)_4$	2.57	0.25	43
$Hg[SC(CH_3)_3]_2$	2.63	-	9
$HgCl_2(C_{12}H_8SO)_2$	3.12	-	-

Compound	Hg-O (Å)	s	Ref
HgO	2.03	0.50	5
Hg_3OCl_4	2.03	0.50	74
$Hg_3O_2Cl_2$	2.16	0.30	73
$HgCl_2.2(C_6H_5)_3AsO$	2.34	0.04	13

Compound	Hg-N (Å)	s	Ref
$Hg(NH_3)_2Cl_2$	2.07	0.50	46
$Hg(C_{15}H_{11}N_4S)_2(C_5H_5N)_2$	2.55	-	32
$Hg(CN)_2$	2.70		

CHAPTER 6

THE STRUCTURES OF TRIHALIDE IONS

6. THE STRUCTURE OF TRIHALIDE IONS

6.1 Introduction.

There exists a large variety of molecules and ions consisting only of halogen atoms. From the simplest species, the halogen molecules, to the complicated polyhalide ions, the subject has been extensively studied from the point of view of their stabilities and structure. A significant part of the field comprises the commonly occurring trihalide ions. Some halide structures are isoelectronic with some neutral rare gas compounds, and this connection lends further interest to the problem of their electronic structure (Rundle,1963). Alternative proposals have been put forward, and owing to the impossibility of detailed theoretical calculation, it would appear that a large body of experimental data is required to come to any firm understanding of the bonding.

All halogen complexes contain an even number of electrons, and are diamagnetic, that is, all neutral species have an even number of atoms, and all singly charged species, an odd number. The stability of the interhalogens, AB, relative to the elements at standard conditions, decreases in the order of decreasing electronegativity difference between A and B. The A-B bond distance is less than the sum of the Pauling

covalent radii of A and B by an amount decreasing with decreasing difference in electronegativity. While the stabilities of the interhalogens AB_3 and AB_5 with respect to the elements follow the same pattern, the stabilities with respect to partial dissociation, and in some cases disproportionation products, must also be considered. Such structures contain unequal bond lengths.

Several trihalide ions have been investigated crystallographically. It is found that all but Br_3^- are linear or nearly so and have bond lengths greater than would be expected on the basis of the sums of the atomic covalent radii. In the heterotrihalide ions the heavier atom always occupies the central position. Trihalides in which the bonds are of equal length, and in which they differ are known. Some polyiodide ions have also been studied, and in some of them, I_3^- units can be distinguished (Havinga and Wiebenga, 1958). The I-I bond lengths are equal in the compound, tetraphenylarsonium tri-iodide, (Mooney Slater, 1959), but unequal when the ion occurs with the small cations NH_4^+ (Mooney, 1935) and Cs^+ (Tasman and Boswijk, 1955), and in CsI4 (Havinga, Boswijk and Wiebenga, 1954). Slightly differing bond lengths occur in the compound $HI_3.2C_5H_5\ CONH_2$ (Reddy, Knox and Robin, 1964). The $[Cl\text{-}I\text{-}Cl]^-$ ion is symmetrical in the presence of

$[(CH_3)_4N]^+$ (Mooney, 1939),
and $[PCl_4]^+$ (Zelezny and Baenziger, 1952), and as in NH_4BrICl, (Mooney, 1938) the bond lengths do not differ greatly from the sums of the atomic covalent radii. In piperazinium bisdichloriodide (Rømming, 1958), however, the I-Cl distances differ sharply, one chlorine atom being closely associated with three nitrogen atoms of the organic group. Finally Br_3^- appears to be bent and unsymmetrical, (Romers and Keulemans, 1958).

In these ions less subject to intensely localised electrostatic forces, the bond lengths are equal, and their structure can be simply explained to some extent on the basis of sp^3d hybridisation of the central atom orbitals (Pauling, 1939). The configuration of the polyhalogen species can be rationalised by the application of the rule that repulsions between lone pair electrons in different orbitals are greater than repulsions between electrons in different bonding orbitals. At the same time, this hybridisation scheme also explains why the heavy halogen atom occupies the central position, since it can more readily make use of its d orbitals.

However, several observations seemed to indicate that this was not entirely correct or at least that another hybridisation scheme would do just as well. NQR studies strongly suggested that the participation of

d orbitals could not be great (Cornwell and Yamasaki,1957). The bond lengths in the symmetrical I_3^- ion are greater than might be expected for sp^3d hybrids, and it seemed unlikely that this could be attributed entirely to electrostatic interaction with the cation. Infra-red studies demonstrated that the stretching force constants in the trihalide ions were far in excess of those in the corresponding simple interhalogens (Person, Anderson and Fordemwalt, 1961), where there is considerably less room for speculation as to the type of bonding. Finally, the energetics of d orbital participation remained in question (Pimentel, 1951).

In defence of the description of the bonding using hybrids of s, p and d orbitals, it is interesting to note the calculations made by Duffy (1949) in a quite different connection. They show that in a pentacovalent molecule with the trigonal bipyramidal configuration, and identical ligands, the axial bonds are weaker and longer than the equatorial ones. He showed that the best hybrids are obtained with the mixing $sp^{1+2n}d^{3-2n}$, where $n = 1$ i/e. The low stretching force constants in PCl_5 have been cited in evidence for this mixing.
Also it has been observed by Bent (1961), that for light atoms the amount of s character in sp^n hybrid orbitals, tends to concentrate in these bonds directed towards the

more electropositive ligands. As has been demonstrated for the case of Hg(II), this is at least one way of usefully correlating a large body of experimental observations for heavy atoms. In the case of the trihalide ions, the equatorial positions in a trigonal bipyramidal arrangement of orbitals on the central atom, are occupied by non-bonding electron pairs. These positions can therefore be considered as being occupied by a very electropositive ligand, and consequently the non-bonding electron pairs possess more s character than the bonding electrons. The long, weak bonds can then be understood as possessing less s character than pure sp^3d hybrids.

An attempt to elucidate the cause of the dissymmetry in some I_3^- ions, was made by Slater (1959), by using as an analogy, the H_3 system intensively investigated by Hirschfelder, Diamond and Eyring (1937). They illustrated the variation in potential energy of the system as the central atom is moved from one terminal atom to the other, the distance, D, between the terminal atoms being held constant. For large separations, D, there are two energy minima as the central atom position is varied, but at small values of D, the two minima coalesce to give one minimum midway between the terminal atoms. On these grounds, Slater argued that there was a critical value

of the terminal atom separation in tri-iodide ions, above which the ion was unsymmetrical, and below which it was symmetrical, The separation was taken to be affected by the environmental forces on the ion. The one case in which a symmetrical I_3^- ion is known, however, is in tetraphenylarsonium tri-iodide, and it can be argued that the cation is not capable of exerting the necessary electrostatic force to constrict the trihalide grouping because its charge is too diffuse and because it is not itself sufficiently rigid. The dissymmetry in the Cs^+ and NH_4^+ compounds is seen as a consequence of these smaller cations allowing the trihalide ion to lengthen. The terminal iodine atom separation in such an ion, would then approach that which would be observed in a free ion.

In a covalent description of the bonding, it is not essential to make use of the d orbitals on the central atom. Suitable molecular orbitals can be constructed from the three atomic p functions, one from each atom (Pimentel, 1951; Havinga and Wiebenga, 1959; Rundle, 1963). The combination results in a bonding, a non-bonding, and an anti-bonding orbital. Placing the sixteen outermost electrons into the six atomic p orbitals and the two lowest molecular orbitals, results in bonds rather weaker than conventional electron pair covalent bonds.

The two molecular orbitals containing four electrons are distributed over all three atoms, but the non-bonding orbital is largely concentrated on the terminal atoms. This hybridisation at once accounts for the long bonds and explains why the more electronegative atoms favour the terminal positions. It has been found that the configurations of interhalogen molecules are correctly predicted by energy calculations using the orbitals. Bond orders of many complexes have also been calculated, and these agree well with the observed bond lengths in all but the Br_3^- ions. The asymmetry of the I_3^- ion in CsI_3 is qualitatively explained.

If a small amount of d character is admitted into this scheme, there is really little difference between the two proposals, assuming that most of the s character resides in the lone pair orbitals. It appears that when the tri-iodide ion is not subjected to intensely localised coulombic forces, it adopts a symmetrical configuration with long bonds containing little d character. Shorter bonds are observed in mixed tri-halides, and before the discussion can be made general, more data are required to confirm the trend, and to separate environmental factors from purely internal electronic factors.

6.2 Solution of the Structure of $(C_6H_5)_3$ $AsBr_2I$.

The compound crystallises in well formed, stable, red needles. From oscillation and precession photographs about their needle axis, they were found to be monoclinic, with cell dimensions, a = 19.48, b = 18.47, c = 12.00 Å, γ = 107.6°, volume = 4115 $Å^3$. The density, calculated on the assumption that there were eight formula units per unit cell, was 2.17 gm. $cc.^{-1}$ Equi-inclination Weissenberg photographs were taken, with the crystal oscillating about its needle axis. From these, the (hk0) reflections were observed to be absent when k was odd. It was also noticed that the intensity was rather low, whenever h was odd. Precession photographs of the zone (0kl), revealed absences in (00l) when l was odd. There were no general absences. The space-group is therefore $P2_1/b$, and there are two formula units per asymmetric unit.

Partial three-dimensional data was obtained by visual estimation of multiple film, equi-inclination, Weissenberg photographs taken with Cu Kα radiation (λ = 1.5418 Å). Iodine has an absorption edge not far from the wave-length of this radiation, and the anomalous scattering gave the photographs a rather high background intensity. As the equi-inclination angle increased, the spot shape varied more with sin θ, and for the last two

layers, corrections were applied by multiplying the intensity by the spot length. At high sin θ values, the intensities of the α_1, α_2 components of the doublet, which were in the ratio of 1:2, were added. The total number of independent reflections is given approximately by the volume of a quadrant of reciprocal space observable with the given radiation, divided by the volume of the reciprocal cell. This is 8.378/0.0008906 = 9407 neglecting systematic halvings. About 60% of these reflections came within the range of the method used. Non-zero values were given to 4363 reflections. A further 1269 were noted to be below the limit of observation.

The scale factors between the films were estimated by making independent measurements of the same reflection on two or three different films. The scale factors obtained were averaged over all pairs of film for any particular layer, and plotted against equi-inclination angle. Theyclosely parallel those calculated by Rossmann.

The data for the layers, l = 0→8 were placed on approximately the same scale by correlation with the $(h\bar{h}l)$ zone intensities, which were visually estimated from timed exposures on a precession camera, using Mo Kα radiation. Data reduction to F^2 was carried out

on a DEUCE computer for the Weissenberg data, and graphically for the precession data. The overall disagreement factor,

$$R = \frac{\sum \sum (K\,|F\ \text{Weiss.}| - |F\ \text{Precession}|)}{\sum |F\ \text{Precession}|}$$

was 0.068. (K is a scale factor).

The thermal motion of the crystal was characteristically slight, for a largely inorganic compound far from its melting point and strong reflections were observed right up to the edge of the film. Although the data extended well beyond the region of reciprocal space observable with Cu Kα radiation, no attempt was made to collect more by using a shorter wavelength or by rotating the crystal about another axis. Refinement by least-squares was envisaged, and truncation of the data does not affect this method. The total number of data collected was such as to allow about twelve observations for every parameter in the structure, assuming anisotropic temperature factors for every atom. The only situation in which the effects of the termination of the data at the eighth layer became apparent, was in the three-dimensional Fourier maps, when there were prominent diffraction ripples in the z-direction, above the heavy atoms.

Solution of the Structure.

The equivalent positions of $P2_1/b$ are:

$$x,y,z;\quad \bar{x},\bar{y},\bar{z};\quad \bar{x},1/2-y,1/2+z;\quad x,1/2+y,1/2-z.$$

The Patterson space group is P^2/m, and the twelve symmetrical, or Harker, peaks, are:

2x, 2y, 2z;	2x, 2y-1/2, 1/2;
2x, 2y, -2z;	2x, 1/2+2y, 1/2;
0, 1/2, 1/2-z;	0, 1/2, 1/2+2z;

and their centrosymmetric equivalents. The unique volume axb/2xc/2 was computed.

Before the systematic analysis of the structure was started, one useful piece of information was obtained from the appearance of the photographs. The reflections, (hk0), were all of low intensity when h was odd. Apart from the space group symmetry (b-glide), this implied a pseudo-translation of a/2 or a pseudo-a-glide. This additional symmetry could have applied to all of the structure approximately, or to some prominent part of the structure only.

The problem consisted of the solution of the Patterson for ten independent heavy atoms, with two particularly heavy atoms to aid the solution. Two approaches to the problem were adopted. The volume

around the origin was scrutinised for an image of a known entity in the structure - that of the trihalide grouping which would be at least approximately linear; and the Harker line and section examined for the iodine peaks.

A peak was found about 2.75 Å from the origin, and co-linear with it and the origin, a second peak a further 2.75 Å away. The peak further from the origin was 3 1/2 times smaller than the first. These heights and positions imply the presence of a linear Br-I-Br ion. Thus the orientation of a major part of the structure had been found.

Two Harker peaks of height more than twice any other at w = 1/2, were found; A and B in figure (14). As a start, these were taken as being the two iodine Harker vectors. The z co-ordinates of the atoms were then sought from the Harker line (0, 1/2, w), figure (15), but this was not really informative. The c axis, being much shorter than the others, the line was overcrowded by peaks, representing the (0, 1/2, $1/2 \pm 2z$) vectors of every atom. We therefore proceeded to the location of the other symmetrical vector peaks for the two independent atoms. The Harker peak A at (0.400, 0.020, 1/2) taken as (-2x, 1/2-2y), had given x = 0.300, y = 0.240. A large peak was found at

(0.597, 0.473, 0.250), and if this is taken as the (2x, 2y, 2z) vector, z = 0.125. The Harker line can now be used as a check on the z co-ordinate. It has a maximum at $1/2 \pm 2z = w = 0.250$. This fixes the magnitude, but not the sign of z, but for the first atom, this is immaterial. The other large peak, B, at (0.172, 0.135, 1/2), was used to derive co-ordinates in a similar manner, giving x = 0.086, y = 0.183 or 1/2-0.183. However, the other symmetrical vector, (2x, 2y, 2z), was not represented by a peak of appropriate size, and the vectors between the independent iodine atoms could not be found. Iodine to iodine interactions are approximately twice as large as interactions involving only bromine or arsenic atoms, and iodine to bromine or iodine to arsenic interactions are about 2/3 of iodine to iodine vectors. So confusion must exist in distinguishing the various types of vectors, since it can reasonably be expected that some double iodine to bromine vectors will be present. The peak B was in fact a combination of peaks.

If it is assumed that the pseudosymmetry detected from the intensities, applies at least approximately to to the iodines, the peak A can be taken as representing both iodine Harker vectors. The co-ordinates of the two independent iodines can be written:

x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\bar{x}, 1/2-y, 1/2+z$; $x, 1/2+y, 1/2-z$;
$1/2+x, y, z'$; $1/2-x, \bar{y}, \bar{z}'$; $1/2-x, 1/2-y, 1/2+z'$;
$1/2+x, 1/2+y, 1/2-z'$.

The cross vectors will therefore be:

(1) $1/2, 0, z'-z$, (2) $1/2+2x, 2y, z'+z$,
(3) $1/2, 1/2, 1/2-z'-z$, (4) $1/2-2x, 1/2-2y, 1/2+z'-z$

There are peaks of appropriate size at (0.897, 0.017, 0.417) and(0.103, 0.480, 0.167) corresponding to (4) and (2) respectively. These yield, for the iodine co-ordinates:

	x	y	z
I	0.300	0.240	0.125
I'	0.800	0.240	0.042

All iodine to iodine vectors were identified, and used to confirm the correctness of these co-ordinates. After the iodines had been located, it was simple to calculate the positions of the bromines attached to them. The location of the remaining four atoms was, however, less straightforward, and recourse was made to three-dimensional superposition by a graphical method. The positions of the eight iodine atoms were marked on a grid representing the unit cell, the origins of eight

Patterson maps placed on these positions, and regions of positive overlap mapped. Actually the superposition was carried out in stages, only two Patterson maps being used simultaneously. This was carried out from z = 0 to z = 1/4 for the whole area of each section. Since there is an image of the structure around every heavy atom and also around the origin, the superposition represents the electron density referred to the same origin as that chosen for the initial atoms. The superposition map was not contoured below a certain arbitrary chosen minimum, in order to reduce the possibility of obtaining spurious peaks due to ripples in the Patterson function. It revealed unambiguously, all ten heavy atom locations, with little or no background, figure (16).

The two sets of five heavy atoms were closely related by the pseudo-glide, so that many peaks in the Patterson were composite. For this reason, it was impossible to deduce very accurate co-ordinates for the heavy atoms, and the pseudosymmetry was initially taken as being exact. The co-ordinates obtained, are shown in table (19).

The co-ordinates were used to calculate structure factors, and the disagreement index:

$$R = \sum \left[k|F_o| - |F_c| \right] \Big/ \sum |F_o| k,$$

was found to be 0.406. The phases of these structure factors were used in computing a F_o fourier, all terms for which $\{ |F_o| - |F_c| \} > |F_o|$, being omitted. Three thousand, one hundred and seventy-one terms were used in the calculation. From the map, improved heavy atom co-ordinates, and co-ordinates of all 36 carbon atoms, were obtained. When these were used in another round of structure factor calculations, the R value dropped by 0.088 to 0.318. Two further cycles of F_o refinement resulted in an improvement in R, to 0.0250 over all 4360 observed terms. By this time, the shifts in the heavy atom co-ordinates were much less than 0.1 Å. Back shift corrections were not calculated owing to the impossibility of performing the long Fourier calculations twice for each cycle. Throughout the solution and preliminary Fourier refinement, the scales of the different zones of F_o were adjusted to make $\sum k|F_o| = \sum |F_c|$. This procedure can be criticised because of interaction between the ks and temperature factors. However, the temperature factors were not altered at this stage, and the Fs had to be 'scaled' to obtain easily an idea whether or not they were correctly-phased. At the final round of Fourier refinement, the observed and calculated scales differed by 12% at worst.

An unique volume of the electron density is either axb/2xc/2 or axbxc/4. Since the Fourier calculations were made in sections normal to the unique axis, the latter volume was chosen to minimise computing time. Initially the independent atoms were referred to this volume rather than to complete molecules. When Fourier refinement was discontinued, the atoms were numbered so that for the heavy atoms, odd numbers refer to one formula unit, and even numbers to the other independent formula unit. Numbers C(1) to C(18) were reserved for light atoms of one unit, and C(19) to C(36) for atoms belonging to the other. The degree to which the two independent units are related by the pseudo-glide, can be seen at a glance from table (19).

The structure is not yet refined.

Figure 14.

$(C_6H_5)_3AsBr_3I$. The three-dimensional Patterson function. Section at w = 1/2, P(u,v,1/2). The contour levels are arbitrary.

Figure 14.

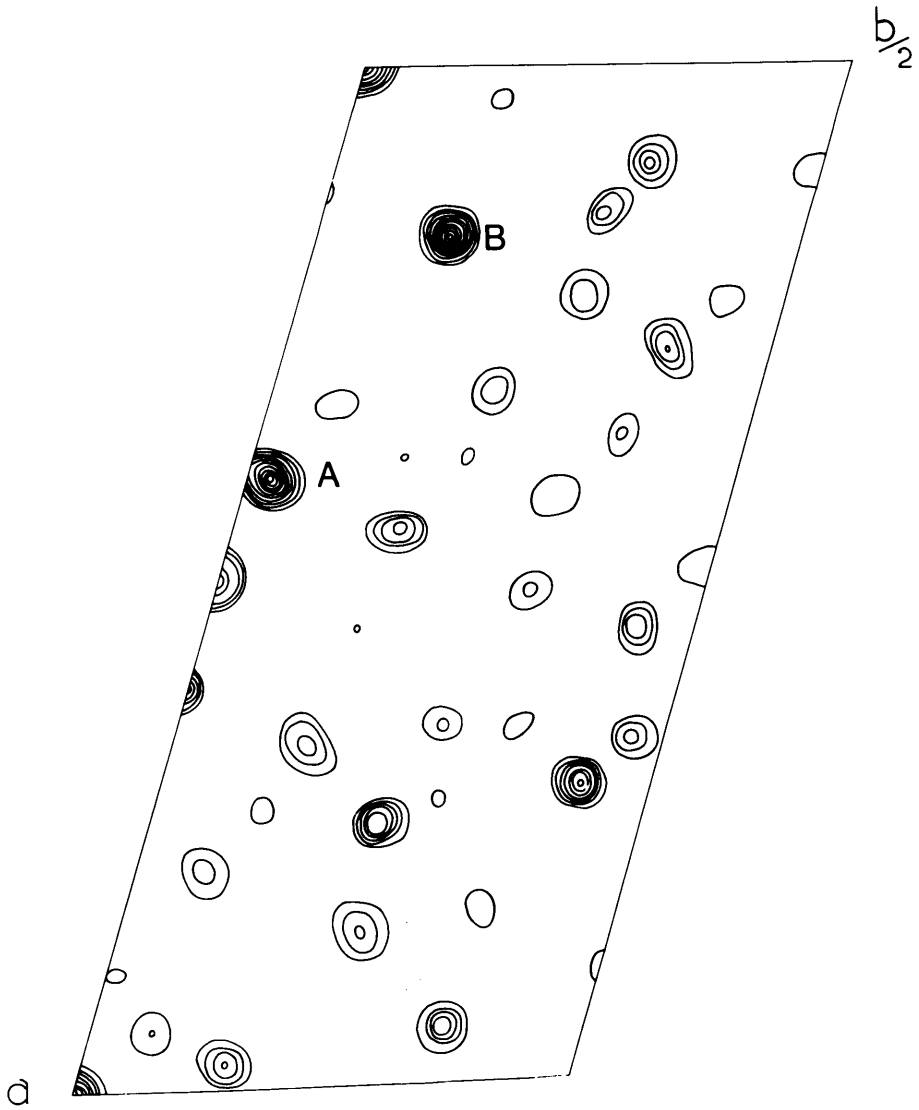


Figure 15.

$(C_6H_5)_3AsBr_3I$. The three-dimensional Patterson function. Line at u = 0, v = 1/2, P(0,1/2,w).

Figure 15.

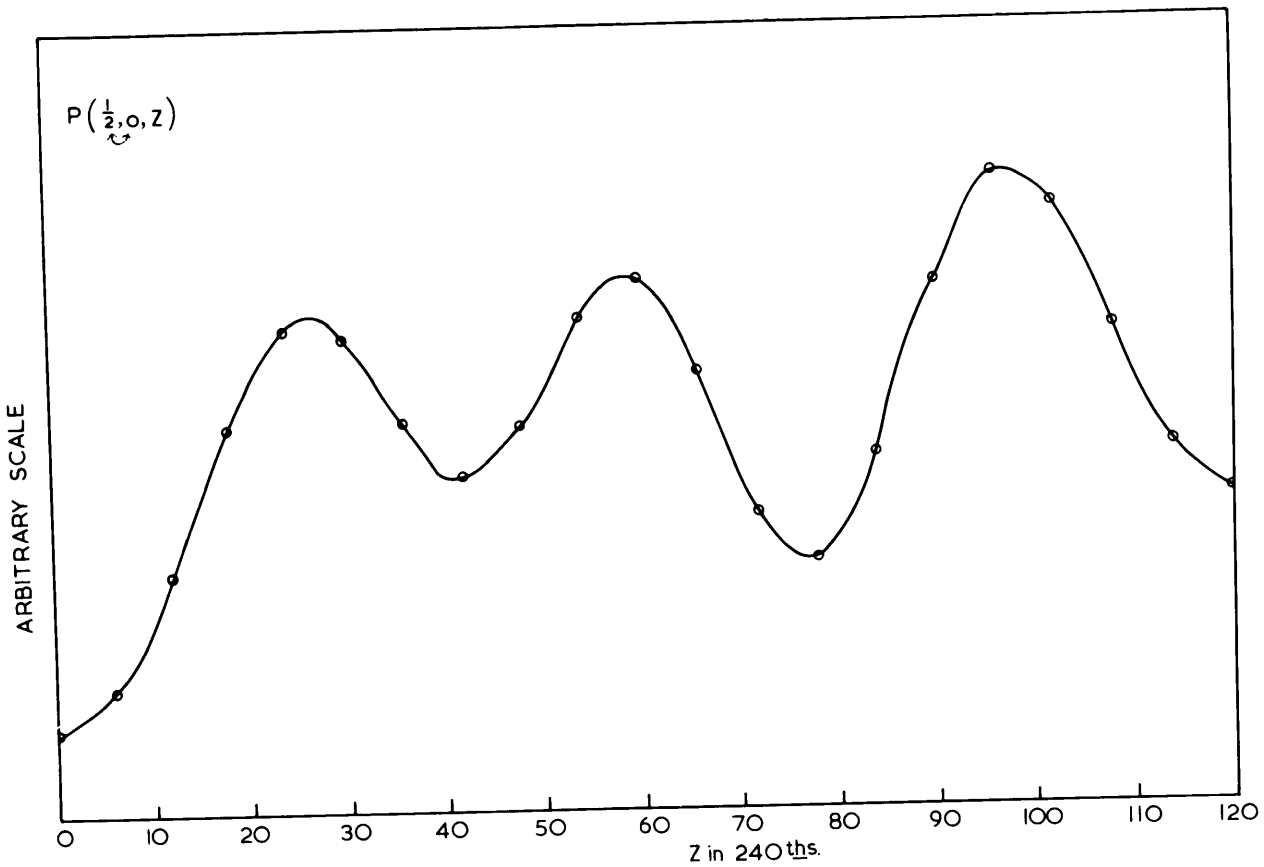

P(½,0,Z)
ARBITRARY SCALE
0
10
20
30
40
50
60
70
80
90
100
110
120
Z in 240ths.

Figure 16.

$(C_6H_5)_3AsBr_3I$. The three-dimensional superposition function projected down the c-axis. The contour levels are arbitrary.

Figure 16.

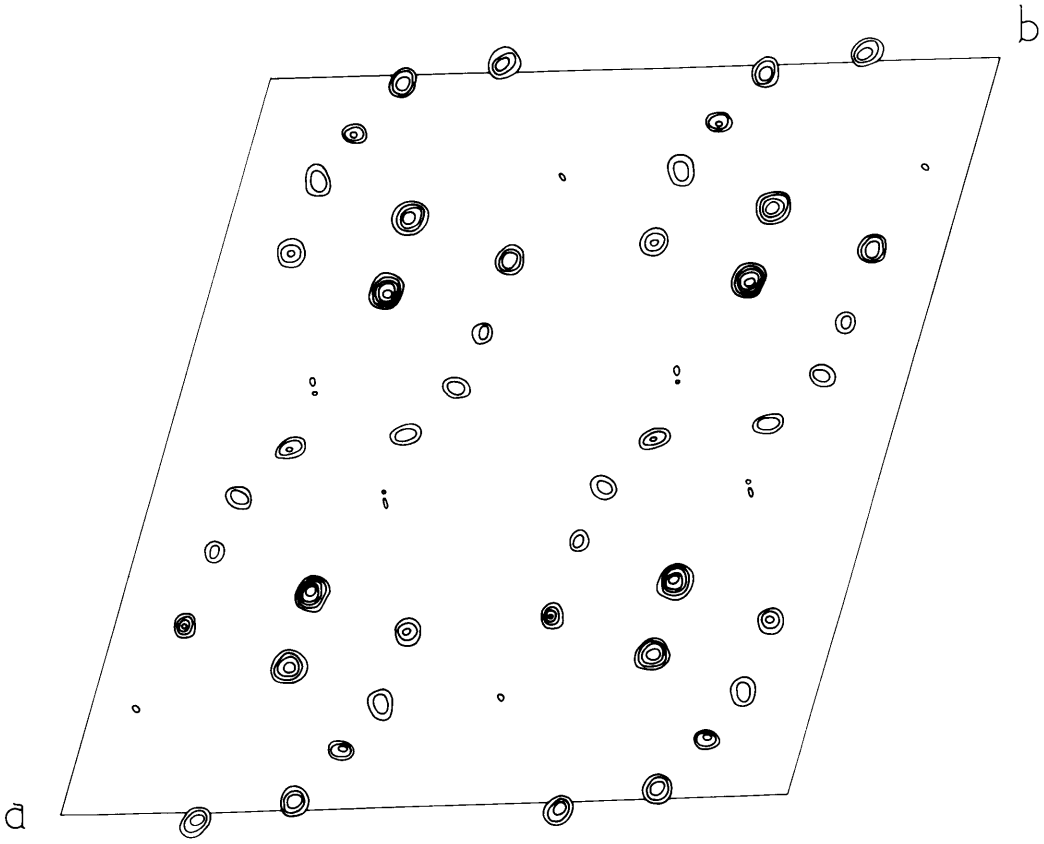


Figure 17.

$(C_6H_5)_3AsBr_3I$. Projection of the structure down the c-axis.

Figure 17.

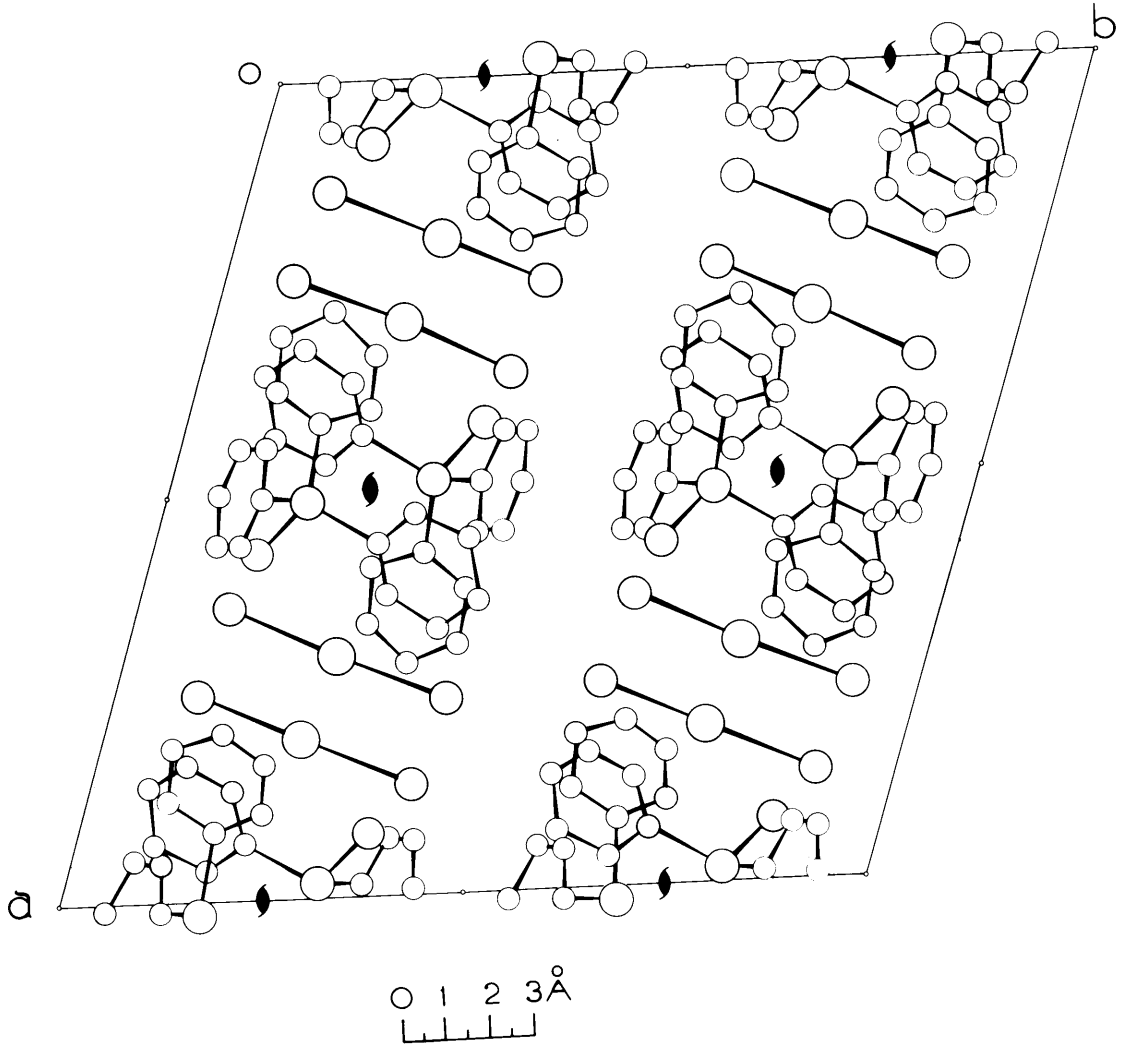


TABLE (19)

$(C_6H_5)_3$ $AsBr_3I$

Fractional Atomic Co-ordinates

Atom	x	y	z
I (1)	.19747	.25378	.54490
I (2)	.29885	.23502	.12704
Br(1)	.13425	.10067	.58027
Br(2)	.24062	.08436	.17186
Br(3)	.25342	.39814	.49010
Br(4)	.36148	.38578	.06526
Br(5)	.07851	.13641	.31512
Br(6)	.42287	.37079	.33750
As(1)	.01647	.18335	.19727
As(2)	.48928	.32537	.46163
C (1)	.01163	.13221	.06042
C (2)	.07143	.11228	.03513
C (3)	.06491	.08040	.91945
C (4)	.00833	.06272	.85892
C (5)	-.05238	.08067	.88537
C (6)	-.04857	.11379	.00026
C (7)	-.08072	.17416	.25653
C (8)	-.12052	.09806	.26874
C (9)	-.18672	.08301	.33318
C(10)	-.20514	.14852	.37159
C(11)	-.16314	.21111	.36819

TABLE (19) (contd)

Atom	x	y	z
C(12)	-.10357	.22324	.30441
C(13)	.06770	.28897	.17476
C(14)	.03444	.32774	.12072
C(15)	.07145	.40243	.07739
C(16)	.14144	.42895	.12397
C(17)	.16743	.38942	.19510
C(18)	.13349	.31921	.21041
C(19)	.50203	.11591	.08378
C(20)	.56747	.10467	.12546
C(21)	.56496	.07859	.25052
C(22)	.50689	.06279	.30383
C(23)	.44515	.07084	.26250
C(24)	.44578	.10485	.16023
C(25)	.41974	.16183	.88550
C(26)	.36935	.09409	.88708
C(27)	.29992	.08712	.85054
C(28)	.28178	.14098	.78535
C(29)	.33951	.21555	.79702
C(30)	.40447	.22712	.85127
C(31)	.56652	.27721	.97464
C(32)	.53247	.31522	.04726
C(33)	.56429	.38733	.07222
C(34)	.64434	.41775	.02698

TABLE (19) (contd)

Atom	x	y	z
C(35)	.67255	.38088	.98620
C(36)	.63145	.30536	.94937

TABLE (20)

$(C_6H_5)_3$ $AsBr_3I$

Bond Lengths (Å)

I (1) - Br(1)	2.75	I (2) - Br(2)	2.72
I (1) - Br(3)	2.64	I (2) - Br(4)	2.78
As(1) - C (1)	1.88	As(2) - C(19)	1.80
As(1) - C (7)	1.98	As(2) - C(25)	1.94
As(1) - C(13)	1.92	As(2) - C(31)	1.88
As(1) - Br(5)	2.20	As(2) - Br(6)	2.29

Average Lengths

I - Br	2.72
As - Br	2.25
As - C	1.90

TABLE (21)

Bond Angles

Br(1) - I (1) - Br(3)	174°	Br(2) - I (2) - Br(4)	176°
C (1) - As(1) - C (7)	112°	C(19) - As(2) - C(25)	113°
C (1) - As(1) - C(13)	109°	C(19) - As(2) - C(31)	117°
C (1) - As(1) - Br(5)	108°	C(19) - As(2) - Br(6)	107°
C (7) - As(1) - C(13)	109°	C(25) - As(2) - C(31)	112°
C (7) - As(1) - Br(5)	111°	C(25) - As(2) - Br(6)	104°
C(13) - As(1) - Br(5)	108°	C(31) - As(2) - Br(6)	101°

Average angle about As = 109°

6.3 Description of the Structure.

The compound consists of the ions $[(C_6H_5)_3AsBr]^+$ and $[BrIBr]^-$. The anion is almost linear. The iodine atom occupies the central position, and there appears to be a slight difference in the I-Br bond lengths. The arsenic of the cation is roughly, tetrahedrally surrounded by three phenyl groups and one bromine atom.

There are two formula units in the asymmetric unit of the cell of symmetry $P2_1/b$. The two independent formular units are closely related by a non-crystallographic a glide plane at z = 0.57. As a result, the two units have almost identical environment, and molecular dimensions are the same in both. A view of the structure projected down [001] is given in figure (17). In projection, the independent trihalide ions lie parallel to one another. A distance of 5.4 Å separates the iodine atoms. Between the extremities of the pairs of anions related by the crystallographic b glide, there is a gap of 4.5 Å, which is very noticable running parallel to the a-axis through the whole structure. The two cations are arranged close to the screw axes between the pairs of anions. Dimensions of the cations are as expected. For example, the average As-C bond length is 1.90 Å, as compared to 1.95 Å found by Mooney Slater (1959) in $(C_6H_5)_4AsI_3$. Averaging the bond distances and

angles in the phenyl rings gives a C-C length of 1.39 Å and a C-C-C angle of 120°. The As-Br length is 2.25 Å.

The most important non-bonded distance is that between a bromine on the anion with one on the cation. The anion is distorted very slightly from a linear configuration, so as to make this distance 3.84 Å. The angle subtended at the anion bromine, -I-Br----Br⁻ is 75°. The shortest non-bonded contact between carbon and heavy atoms is 3.7 Å.

At this stage it is impossible to assert that the differences in Br-I bond lengths in the anion are significant. These bond lengths do, however, seem to be substantially greater than the sum of the covalent radii. It is interesting to compare them with those in ions in similar environments. As was pointed out earlier, the A-B bond distances in the simple interhalogens AB, are less than the sums of the Pauling covalent radii of A and B, by an amount decreasing with decreasing electronegativity difference between A and B. In the case of the trihalide ions then, we might expect that the A-B bond distances would be greater than the sums of the covalent radii, by an amount increasing with decreasing electronegativity difference between the component atoms. The experimental data is rather sparse. The I-I distance in the trihalide ion in $(C_6H_5)_4AsI_3$

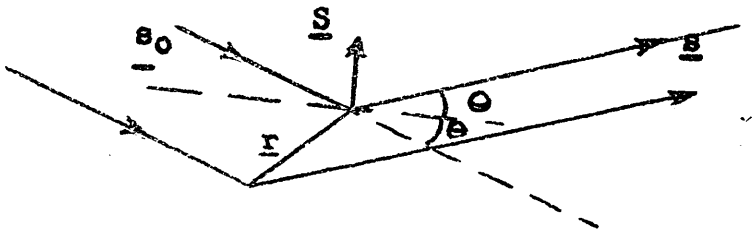
(Mooney Slater, 1959) is 2.90 Å, compared with the sum of radii of 2.66 Å; a difference of 0.24 Å. In the structure described here, the average I-Br distance is 2.72 Å, and the sum of radii, 2.47 Å, giving a difference of 0.25 Å. Finally in the Cl-I-Cl ion in $[(CH_3)_4N][ICl_2]$ and $[PCl_4][ICl_2]$, the bond length is 2.33 Å, which is not significantly different from the sum of the radii (2.32 Å). When unsymmetrical tri-iodide ions are included in the comparison, the expectation may be realised. The average I-I distance in CsI_3 is 2.93 Å, and in NH_4I_3 2.96 Å, giving differences of 0.27 Å and 0.30 Å from the sum of radii.

It appears from these figures, that the BrIBr ion resembles the tri-iodide ion more than the ClICl. It also differs sharply from the anion in $[NH_4][BrICl]$, in which the I-Br bond distance is 2.50 Å.

APPENDIX

APPENDIX

X-rays are scattered by electrons, and for the purpose of X-ray analysis, a body can be described by its electron density distribution; $p(\underline{r})$, where $\underline{r}$ is a vector. Consider monochromatic radiation of wavelength λ, incident on a body from a direction given by a vector $\underline{s}_0$, to be scattered through an angle 2θ. Let the direction of the scattered radiation be given by a vector $\underline{s}$, and let $|s_0| = |s| = 1/\lambda$.



The path difference between a ray scattered from a point $\underline{r}$, and a ray scattered from another point taken as the origin, is $\underline{r}\cdot(\underline{s}-\underline{s}_0) = \lambda\,\underline{r}\cdot\underline{S}$. The phase difference is, therefore, $2\pi/\lambda \times \lambda\,\underline{r}\cdot S = 2\pi\underline{r}\cdot\underline{S}$. If the volume element of the space of $\underline{r}$ is dV_r, the electron content at $\underline{r}$, is $p(\underline{r})\,dV_r$, and the scattered beam is totally described by:

$$p(\underline{r})\,dV_r \exp(2\pi i\,\underline{r}\cdot\underline{S}).$$

The scattering from the whole body is therefore,

$$G(\underline{S}) = \int p(\underline{r}) \exp 2\pi i\,\underline{r}\cdot\underline{S}\; dV_r$$

If $p(\underline{r})$ is a three-dimensional, periodic function, points of identical electron density are given by the

vectors,

$$\underline{r} = u\underline{a} + v\underline{b} + w\underline{c},$$

where u, v and w are integers, and the vectors $\underline{a}$, $\underline{b}$ and $\underline{c}$ define the periodicity. In order that the waves scattered by adjacent identical points will be in phase, the path differences between them must be a whole number of wavelengths.

$$\text{i.e.} \qquad \lambda\, \underline{r}.\underline{S} = n\lambda \qquad n \text{ is an integer;}$$

$$\therefore \qquad (u\underline{a} + v\underline{b} + w\underline{c}) . \underline{S} = n$$

$$\underline{a} . \underline{S} = h$$

$$\underline{b} . \underline{S} = k \qquad (A)$$

$$\underline{c} . \underline{S} = l$$

where h, k and l are integers.

Each of these equations (A) defines a set of equi-spaced planes in the space of $\underline{S}$, and the three sets of planes define a lattice, which can be specified by three vectors, $\underline{a}^*$, $\underline{b}^*$, and $\underline{c}^*$. A point in the lattice is specified by the integer triplet hkl. These integers are identical with the Miller indices of the plane producing the hkl reflection (Bragg).

If the electron density can be considered as being made up of N discrete atoms at positions $\underline{r_n}$ in an unit cell of a crystal, the scattering from the n th atom is given by

$$G_n(\underline{S}) = \int p(\underline{r}) \exp 2\pi i\, (\underline{r}+\underline{r_n}) . \underline{S}\, dV_r,$$

where $p(\underline{r})$ now describes the electron distribution within an atom with respect to its centre.

$$\therefore \quad G_n(\underline{S}) = \left[\int p(\underline{r}) \exp 2\pi i\, \underline{r}.\underline{S}\, dV_r\right] \exp 2\pi i\, \underline{r_n}.\underline{S}$$

$$= f_n(\underline{S}) \exp 2\pi i\, \underline{r_n}.\underline{S}$$

The function $f_n(\underline{S})$, the atomic scattering factor, is a function of the electron distribution of the atom, and can therefore only be known approximately for atoms other than hydrogen. Atomic scattering factors based on self-consistent or variational wave functions have been used where possible in this thesis. They are listed in 'International Tables for X-Ray Crystallography' Volume III.

If the n th atom is at $\underline{r_n} = x_n\underline{a} + y_n\underline{b} + z_n\underline{c}$, where x_n, y_n, z_n are the fractional co-ordinates of the atom refered to the unit cell axes, the total scattering from the unit cell is:

$$G(\underline{S}) = \sum_{n=1}^{N} f_n(\underline{S}) \exp 2\pi i\, (x_n\underline{a}.\underline{S} + y_n\underline{b}.\underline{S} + z_n\underline{c}.\underline{S}).$$

$$G(\underline{S}) = \sum_{n=1}^{N} f_n(\underline{S}) \exp 2\pi i\, (hx_n + ky_n + lz_n).$$

This quantity, only finite at the points given by the Laue equations (A), is the structure factor for a particular set hkl.

The expression,

$$G(\underline{S}) = \int p(\underline{r}) \exp 2\pi i\, \underline{r}.\underline{S}\, dV_r$$

is the Fourier transform of the electron density, so

$$p(\underline{r}) = \int G(\underline{S}) \exp -2\pi i\, \underline{r}.\underline{S}\, dV_s \qquad (B)$$

where dV_s is the volume element in the space of $\underline{S}$.

$p(\underline{r})$ can be represented by a Fourier series.

$$p(\underline{r}) = \sum_{\underline{H}'} F(\underline{H}') \exp 2\pi i\, \underline{r}.\underline{H}'$$

if $p(\underline{r})$ is periodic, so that $G(\underline{S})$ is discontinuous,

$$G(\underline{S}) = \int [\sum_{\underline{H}'} F(\underline{H}') \exp 2\pi i\, \underline{r}.\underline{H}'] \exp 2\pi i\, \underline{r}.\underline{S}\, dV_r$$

This is zero unless $\underline{H}' = -\underline{S}$, in which case,

$$G(\underline{S}) = \int F(H')\, dV_r = V\, F(\underline{H}')$$

$$\therefore \quad p(\underline{r}) = 1/V \sum_{\underline{S}} G(\underline{S}) \exp -2\pi i\, \underline{r}.\underline{S},$$

where V is the volume of the unit cell.

Atoms in Thermal Vibration.

The scattering factor of an atom executing isotropic, harmonic vibration, is the product of the scattering factor of the atom at rest, $f(\underline{S})$, and the transform of the function describing the state of motion of the atom. The latter is a gaussion:

$$t(x) = (2\pi^2 U)^{-3/2} \exp(-x^2/2U),$$

where x is the displacement from the mean position, and U is the mean square amplitude of vibration. Its transform is

$$q(\underline{S}) = \exp\,(-2\pi^2\, U|\underline{S}|^2)$$

Now $|\underline{S}| = 2 \sin\theta/\lambda$, and writing $B = 8\pi^2 U$, the equation becomes

$$q(\underline{S}) = \exp\,(-B(\sin\theta/\lambda)^2).$$

B is the isotropic temperature factor.

In an anisotropic, harmonic, potential field, the vibrations of an atom are described by six independent quantities U_{ij}, such that the mean square amplitude of vibration in the direction of the unit vector $\underline{l}$, is

$$U = \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij}\, l_i\, l_j.$$

The transform of the function describing the motion now is

$$q(\underline{S}) = \exp\,[-2\pi^2(\sum_i \sum_j U_{ij}\, S_i\, S_j)]$$

In the case of an atom in a crystal, the value of q at the reciprocal latice point ha^*, kb^*, lc^*, is:

$$q(hkl) = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}khc^*a^* + 2U_{12}hka^*b^*)]$$

where a^*, b^* and c^* are the reciprocal cell constants. These U_{ij} are the quantities usually given to describe anisotropic temperature motion. Their units are $\mathring{A}^2$, since a^* etc are in $\mathring{A}^{-1}$.

The experimentally measurable integrated intensity I(hkl) of a reflection is related to the structure factor G(hkl) = G($\underline{S}$), by the equation:

$$I = L.P.\ GG^*.$$

P is a factor allowing for the non-polarized state of the X-rays.

$$P = \frac{1 + \cos^2 2\theta}{2}$$

L, the Lorentz factor, depends on the motion of the crystal during data collection. For the equi-inclination Weissenberg method,

$$L = \frac{(\cos^2\mu - \cos^2\theta)^{1/2}}{\sin\theta},$$

where μ is the angle between the axis of rotation of the crystal, and the incident X-ray beam (Tunell, 1939).

If the quantities $G(\underline{S})$ in equation (B) are known completely, the electron density can be calculated by Fourier transformation. Methods of solving crystal structures fall into two catagories, those which have as their initial object, calculation of the experimentally indeterminate phases of the G s, and those which seek to locate atomic centres by other means. If $p(\underline{r})$ is centrosymmetric, the phases of G are restricted to 0^c or π^c provided the origin of co-ordinates is taken to be at a centre of symmetry.

The method of solution used in this thesis is a real space method.

Although $p(\underline{r})$ cannot be directly obtained if the phases of the G s are unknown, it is possible to calculate the transform of the intensity distribution. This function, the self-convolution of the electron density, is that defined by Patterson

$$P(\underline{U}) = \int p(\underline{r})p(\underline{r}+\underline{U})\ V d\underline{r} \qquad (C)$$

Now $$p(\underline{r}) = 1/V \sum_S G(\underline{S}) \exp -2\pi i\ \underline{r}.\underline{S}$$

and

$$\underline{U} = u\underline{a} + v\underline{b} + w\underline{c}$$

$$\underline{r} = x\underline{a} + y\underline{c} + z\underline{c}$$

$$\underline{S} = h\underline{a}^* + k\underline{b}^* + l\underline{c}^*,$$

where u, v, w, x, y and z are fraction co-ordinates, and hkl integers.

$$\therefore \quad P(\underline{U}) = 1/V \iiint \left[\sum_{\underline{S}} \sum_{\underline{S}'} [G(\underline{S}) \exp - 2\pi i \, \underline{r}.\underline{S}] \right.$$

$$\left. \times [G(\underline{S}') \exp - 2\pi i \, \underline{r}.\underline{S}'] [\exp -2\pi i \, \underline{U}.\underline{S}] d\underline{r} \right.$$

This is zero unless $\underline{S} = -\underline{S}'$, in which case,

$$P(\underline{U}) = 1/V \sum_{\underline{S}} G(\underline{S}) \; G(-\underline{S}) \exp -2\pi i \, \underline{U}.\underline{S}$$

$$\text{or } P(uvw) = 1/V \sum_{h} \sum_{k} \sum_{l} G^2(hkl) \exp -2\pi i(hu+kv+lw). \qquad (D)$$

The meaning of the function is clear from equation (C). If the electron density is thought of as being composed of discrete atoms at $\underline{r}_n$, the $P(\underline{U})$ is non-zero when $\underline{U}$ is an interatomic vector. The size of a maximum in $P(\underline{U})$ is proportional to the product of the atomic numbers of the atoms corresponding to the vector $\underline{U}$.

When the crystal has symmetry, the expression (D) simplifies, and maxima corresponding to symmetry related atoms may occur on special lines or planes. The examination so-called Harker lines, peaks and sections is a vital stage in the recovery of the structure from the Patterson. Normally, for a structure of even moderate complexity, the problem is too difficult to solve unless some simplifying feature is present. Simplification is obtained by having a small

number of atoms in the structure of much higher atomic number than the others, The Patterson maxima involving these atoms have then much higher weight than others, and are therefore readily distinguished. Even so, only partial solution may be obtained, and it may have to be assumed that the phases calculated from knowledge of a major part of the structure, approximate sufficiently closely to the true phases, for the remainder of the structure to be found by Fourier methods.

When the structure parameters p_i differ by small amounts e_i from their true values, it is possible to systematically vary the parameters in such a way as to minimise the disagreement between the observed and calculated structure factors. The function of this disagreement, which is minimised in the refinements described in this thesis is:

$$R = \sum_{hkl} w(hkl)(|F_o| - |F_c|)^2$$

where w is a weight. The summation extends over all observed independent planes.

Minimising R with respect to the N parameters, implies that:

$$\frac{\partial R}{\partial p_j} = 0 \qquad \text{for} \quad j = 1, \ldots, N.$$

$$\text{i.e.} \sum_{hkl} \left[w \frac{d|F_c|}{dp_j} \cdot (|F_o| - |F_c|) \right] = 0 \quad \text{for } j = 1, \ldots, N.$$

Since e_i is small,

$$\Delta(p+e) = \Delta(p) - \sum_{i=1}^{N} e_i \frac{d|F_c|}{dp_i},$$

where $\Delta(p+e)$ denotes $(|F_o| - |F_c|)$, which is a function of all the p s, and e s necessary to correct the p s.

$$\therefore \sum_{hkl} w \Delta \frac{d|F_c|}{dp_j} = \sum_{i=1}^{N} \left[\sum_{hkl} w \frac{d|F_c|}{dp_i} \cdot \frac{d|F_c|}{dp_j} \right] e_i$$

$$\text{i.e.} \quad \sum_{i=1}^{N} a_{ij} e_i = b_j \qquad \text{for } j = 1, \ldots, N.$$

where $$a_{ij} = \sum_{hkl} w \frac{d|F_c|}{dp_i} \cdot \frac{d|F_c|}{dp_j}$$

and $$b_j = \sum_{hkl} w \Delta \frac{d|F_c|}{dp_j}$$

These N equations are called the normal equations.

Their solutions are:

$$e_i = \sum_{j} a_{ij}^{-1} b_j$$

where a_{ij}^{-1} is an element of the matrix inverse to a_{ij}.

After refinement on DEUCE, e.s.d s were calculated by hand using the expression:

$$\sigma^2(p_i) = a_{ii}^{-1} \sum w \Delta^2 / m-n.$$

If the errors in the atomic co-ordinates can be taken to be isotropic, the e.s.d. of a bond length d between atoms 1 and 2 is given by:

$$\sigma^2(d) = \sigma^2(1) + \sigma^2(2)$$

In cases where the standard deviations are anisotropic, the formula used was:

$$\sigma^2(d) = \sum_{i=1}^{3} l_i^2 (\sigma_i^2(1) + \sigma_i^2(2)),$$

where l_i is the i th component of the normalised vector in the direction of the bond between 1 and 2.

The standard deviation of an angle θ subtended at atom 2 by the bonds of lengths d_1 and d_3 from atoms 1 and 3, is in the isotropic case:

$$\sigma^2(\theta) = \frac{\sigma^2(1)}{d_1^2} + \frac{d_{13}^2}{d_1^2 d_2^2} \sigma^2(2) + \frac{\sigma^2(3)}{d_3^2},$$

where d_{13} is the distance between atoms 1 and 3.

In the anisotropic case, the formula used was that given by Darlow (1960):

$$\sigma^2(\theta) = \left(\frac{1}{d_1 d_3 \sin\theta}\right)^2 \left[A_3^2\sigma^2(x_1)+(A_1+A_3)^2\sigma^2(x_2)+A_1^2\sigma^2(x_3)\right]$$

+ similar terms in y and z.

Here

$$A_1 = d_1 (\cos\alpha_1 - \cos\theta \cos\alpha_3)$$
$$A_3 = d_3 (\cos\alpha_3 - \cos\theta \cos\alpha_1)$$
$$B_1 = d_1 (\cos\beta_1 - \cos\theta \cos\beta_3)$$
$$\text{etc.,}$$

where $\cos\alpha_1$, $\cos\beta_1$, $\cos\gamma_1$, are the direction cosines of the bond between atoms 1 and 2, and $\cos\alpha_3$, $\cos\beta_3$, $\cos\gamma_3$ are the direction cosines of the bond between 2 and 3.

Both these formulae refer to orthogonal axes.

REFERENCES

REFERENCES

1. Ahrland, S. (1956). Acta Chem.Scand.10, 723.

2. Ahrland, S., Chatt, J. and Davies, N.R. (1958). Quart. Rev. 12, 265.

3. Arkishin, P.A., Spiridinov, V.P. and Khodchenkov,A.N. (1959). Zhur. Fiz. Khim. 33, 20

4. Aurivillius, K. (1950). Acta Chem. Scand. 4, 1413.

5. Aurivillius, K. (1956). Acta Chem. Scand. 10, 852.

6. Benesi, H.A. and Hildebrand, J.H. (1949). J. Amer. Chem. Soc. 71, 2703

7. Bent, H.A. (1961). J. Inorg. Nucl. Chem. 19, 43.

8. Brackman, W. (1949). Rec. Trav. Chim. 68, 417.

9. Bradley, D.C. and Kunchur, N.R. (1964). Nature. 204, 468.

10. Braekken, H. and Scholton, W. (1939). Z.Krist. 89, 448.

11. Braibanti, and Fava, (1959). Z. Krist. 111, 385.

12. Brodersen, v.K. (1955). Acta Cryst. 8, 723.

13. Branden, C-I. (1963). Acta Chem. Scand. 17, 1363.

14. Branden, C-I. (1964a). Arkiv. Kemi. 22, 485.

15. Branden, C-I. (1964b). Arkiv. Kemi. 22, 501.

16. Burnbank, R.D. and Bensay, F.N. (1957). J. Chem. Phys. 27, 981.

17. Busing, W.R., Martin, K.O. and Levy, H.A. (1962). 'A Fortran Crystallographic Least-Squares Program'. Oak Ridge National Laboratory.

18. Cheung, K.K., McEwen, R.S. and Sim, G.A. (1965). Nature. 205, 383.

19. Cornwell, C.D. and Yamasaki, R.S. (1957). J.Chem.Phys. 27, 1060.

20. Cotton, F.A. (1960). J. Chem. Soc. 5269.

21. Damm, K. and Weiss, A. (1955). Z.Naturforsch. 10b, 535.

22. Darlow, S.F. (1960). Acta Cryst. 13, 683.

23. Deacon, G.B. (1963). Rev. Pure Appl. Chem. 13, 189.

24. Duffy, G. (1949). J. Chem. Phys. 17, 196.

25. Fenn, R.H., Oldham, J.W.H. and Phillips, D.C. (1963). Nature. 198, 381.

26. Ginn, S.G.W. and Wood, J.L. (1965). Chem.Communications 12, 262.

27. Gordy, W. and Sheridan, J. (1954). J. Chem. Phys. 22, 92.

28. Gorskii, V. (1934). Physik. Z. Sowjetunion. 5, 367.

29. Grdenic, D. (1950). Arkiv. Kemi. 2, 14.

30. Grdenic, D. and Krstanovic, I. (1955). Arkiv. Kemi. 27, 143.

31. Grdenic, D. (1965). Quart. Rev. To be published.

32. Harding, M.M. (1958). J. Chem. Soc. 4136.

33. Harmsen, E.J. (1938). Z. Krist. 100, 208.

34. Hassel, O. and Hvoslef, J. (1954). Acta Chem. Scand. 8, 1953.

35. Havinga, E.E. and Wiebenga, E.H. (1958). Acta Cryst. 11, 733.

36. Havinga, E.E. and Wiebenga, E.H. (1959). Rec. Trav. Chim. 78, 724.

37. Havinga, E.E., Boswijk, K.H. and Wiebenga, E.H. (1954). Acta Cryst. 7, 487.

38. Hirschfelder, J., Diamond, H. and Eyring, H. (1937). J. Chem. Phys. 5, 695.

39. Huggens, M.L. and Magill, P.L. (1927). J. Amer. Chem. Soc. 49, 2357.

40. Jeffreys, J.A.D., Sim, G.A., Burnell, R.H., Taylor, W.I., Corbett, R.E., Murray, J. and Sweetman, B.J. (1963). Proc. Chem. Soc. 171.

41. Johannson, A. (1939). Arkiv. Kemi., Min. Geol. 13A, No.14.

42. Knobler, C.B., Yoshihara, O. and Pepinoki, R. (1959). Z. Krist. 111, 385.

43. Korczynski, A. (1964). 'Theory and Structure of Complex Compounds'. Ed. B. Jezowska-Trzebiatowska. Pergamon Press, London.

44. Kunchur, N.R. and Truter, M.R. (1958a). J. Chem. Soc. 2551.

Kunchur, N.R. and Truter, M.R. (1958b). J. Chem. Soc. 3478.

45. Leonard, N.J. and Sutton, L.E. (1948). J. Amer. Chem. Soc. 70, 1564.

46. MacGillavry, C.H., de Wilde, J.H. and Bijvoet, J.M. (1938). Z. Krist. 100, 212.

MacGillavry, C.H., de Wilde, J.H. and Bijvoet, J.M. (1936). Z. Krist. 94, 231.

47. Mooney, R.C.L. (1935). Z. Krist. 90, 143.

48. Mooney, R.C.L. (1938). Z. Krist. 98, 324.

49. Mooney, R.C.L. (1939). Z. Krist. 100, 519.

50. Mooney, R.C.L. (1940). J. Amer. Chem. Soc. 62, 2955.

51. Mooney Slater. (1959). Acta Cryst. 12, 187.

52. Mulliken, R.S. (1950). J. Amer. Chem. Soc. 72, 600.

53. Mulliken, R.S. (1952a). J. Phys. Chem. 56, 801.

54. Mulliken, R.S. (1952b). J. Amer. Chem. Soc. 74, 811.

55. Murrell, J.N. (1961). Quart. Rev. 15, 191.

56. Nardelli, M., Briabanti, A. and Fava, e.G. (1957). Gazz. Chim. Ital. 87, 1209.

57. Nardelli, M. and Fava, e.G. (1959). Acta Cryst. 12, 727.

58. Nyholm, R.S. (1961). Proc. Chem. Soc. 273.

59. Orgel, L.E. (1954). Quart. Rev. 8, 422.

60. Orgel, L.E. (1958). J. Chem. Soc. 4186.

61. Pauling, L. (1939). 'Nature of the Chemical Bond'. Cornell Univ. Press, Ithaca, N.Y.

62. Person, W.B., Anderson, G.R. and Fordemwalt, J.N. (1961). J. Chem. Phys. 35, 908.

63. Pimentel, G.C. (1951). J. Chem. Phys. 19, 446.

64. Reddy, M.J., Knox, K. and Robin, M.B. (1964). J. Chem. Phys. 40, 1082.

65. Robertson, J.M. and Woodward, (1940). J. Chem. Soc. 36.

66. Robertson, J.M. (1943). J. Sci. Instr. 20, 175.

67. Robin, M.B. (1964). J. Chem. Phys. 40, 3369.

68. Romers, C. and Keulemans, E.W.M. (1958). Proc. Koninkl. Ned. Akad. Wetenschap. B61, 345.

69. Rossmann, M.G. (1956). Acta Cryst. 9, 819.

70. Rundle, R.E. (1961). Acta Cryst. 14, 585.

71. Rundle, R.E. (1963). J. Amer. Chem. Soc. 85, 112.

72. Rømming, C. (1958). Acta Chem. Scand. 12, 668.

73. Scavincar, S. (1955). Acta Cryst. 8, 379.

74. Scavincar, S. and Grdenic, D. (1955). Acta Cryst. 8, 275.

75. Scavincar, S. and Grdenic, D. (1964). Acta Chem. Scand. 18, 1327.

76. Slater, J.C. (1959). Acta Cryst. 12, 197.

77. Struchkov, Yu.T., Kitajgorodskij, A.I. and Khotsyanova, T.L. (1953). Doklady Acad.Nauk.SSSR.93,675.

78. Tasman, H.A. and Boswijk, K.H. (1955). Acta Cryst. 8, 59.

79. Truter, M.R. (1963). J. Chem. Soc. 1309.

80. Tunell, G. (1939). Amer. Min. 24, 448.

81. Wells, A.F. (1937). Z. Krist. 96, 435.

82. Wells, A.F. (1962). 'Structural Inorganic Chemistry', Clarendon, Oxford, 3rd. ed., 892.

83. White, J.G. (1963). Acta Cryst. 16, 397.

84. White, N.E. and Clews, C.J.B. (1956). Acta Cryst. 9, 586.

85. Zaslow, B. and Rundle, R.E. (1957). J. Phys. Chem. 61, 490.

86. Zelezny, W.F. and Baenziger, N.C. (1952). J. Amer. Chem. Soc. 74, 6151.

87. Zhdanov, Z.V. and Sanadse. (1952). Zhur. Fiz. Khim. 26, 469.

88. Zhdanov, Z.V. and Zvonkova, Z.V. (1957). Acta Cryst. 10, 29.

89. Zvonkova, Z.V., Samodurova, V.V. and Vorontsova, L.G. (1955). Doklady Akad. Nauk. SSSR. 102, 1115.

90. Zvonkova, Z.V. and Zhdanov, G.S. (1952). J. Fiz. Khim. URSS. 26, 586